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CONTENTS

	PAGE
Gasoline Loss Control and Molecular Weight Determinations. By H. G. Koefoed	529
Some Observations on the Development of Extreme Pressure (E.P.) Properties by Chlorine and Sulphur Additives in Mineral Oil, as Assessed by the Four Ball Machine. By W. Davey	575
Researches on Asphaltenes. Part II. Radical Reactions. By F. J. Nellensteyn and J. Dorleyn . . .	582
Abstracts	269A
Books Received	316A
Institute Notes	i-vi

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VOL. 32. No. 273. SEPTEMBER 1946

GASOLINE LOSS CONTROL AND MOLECULAR WEIGHT DETERMINATIONS.

By H. G. KOEFOED, D.Sc. (Fellow).

ALL handling of gasoline during refining, storage, transport, or distribution causes loss which may be large or small, according to the method of handling, the quality of the gasoline, and the efficiency of control. It is desirable to reduce the amount lost to the minimum.

Loss figures are the differences over given periods between quantities received and delivered, adjusted for changes in stocks, the overall losses being the total of the losses sustained at the various points. These may be expressed in terms of volume, weight or cash value, or as a percentage of total throughput. If the latter figure does not exceed 1·5 per cent the loss is normal for proper equipment carefully used.

The accounts will show at what stage the greatest losses are incurred, but methodical investigation is needed to trace causes and effect reduction. Separate study of the various sources of loss will give their relative importance and allow consideration of the fundamental problem: How can the losses be reduced without expensive alterations to existing equipment?

Whenever gasoline is handled there will be an evaporation loss; every change in temperature causes an increase or decrease in volume, and every measuring out leads to commercial loss. There may also be loss arising from waste and negligence.

Causes of loss may be summarized as follows:

- Total leakage
  - Ocean leakage
  - Ocean depot
    1. Evaporation loss.
    2. Temperature loss.
    3. Gauging loss.
    4. Waste.
  - Distribution depot
    1. Evaporation loss.
    2. Temperature loss.
  - Transportation
    3. Waste.

While the above might be made more detailed by subdividing the various losses, it must be borne in mind that too much detail often tends to blur the whole.

LOSS THROUGH WASTE AND NEGLIGENCE.

The most conspicuous loss is the loss through waste and negligence. It should not be difficult to explain to operators that waste means loss, and

that a leak of one drop of gasoline a second from pipeline flanges, etc., means a total waste of 1,500 litres a year.

Special attention must be given to the possibilities of hidden leaks. Underground pipes and tanks, and tank bottoms must be built with great care, and of first-class materials, and protected in the best possible way. Tank bottoms and covered parts should be examined whenever possible and pressure tests of subterranean pipes should be made at regular intervals. The testing pressure should be considerably higher than the highest working pressure. It is more economical to burst a pipe when testing it, and to renew it six months before the normal time, than to have a leaky pipe. A subterranean leak may waste considerable quantities of gasoline before it is discovered.

Suitable equipment, in good condition and carefully operated is necessary if loss through waste and negligence is to be avoided completely.

The fact that waste also increases the fire risk is a point which may be used advantageously in the education of operators.

Gauging Losses.

Losses which result from gauging are much more difficult to reduce. In Denmark all sales measures must be legally gauged to show a positive margin within 0·5 per cent. All gasoline sold, whatever the method of delivery, must, therefore, show the same margin as the sale-gauges, and consequently the loss from gauging cannot be brought down to nil. By special care in the manufacture of measuring apparatus the surplus legally stipulated can be kept at the lowest permissible level, and it is possible to reduce this loss to less than 0·2 per cent, while, if no special precautions are taken, it is usually 0·3 per cent or more.

Loss from gauging is only mentioned in the scheme above under the heading ocean depots, as in the organization under investigation the quantity of benzine which the distribution depots receive from the ocean depots contains the surplus required for further dealings.

Although the quantity saved may appear insignificant, it may, however, amount to 5 to 10 per cent of the total leakage.

Temperature Loss.

As the temperature expansion coefficient of gasoline is high, approximately 0·0011 per °C., changes in temperature are of great influence. In the summer-time the temperature of gasoline arriving in a tanker will, owing to the cooling effect of the sea water, be lower than the average temperature at which it is delivered from the installation, a fact which results in an excess quantity. This excess may not compensate for the deficiency arising during the colder period of the year, in those countries where gasoline is imported from countries having a considerably higher average temperature.

Loss through change of temperature occurs both at the ocean depot and at the distribution depot, as well as in course of transportation, and cannot be counteracted effectively.

Evaporation Loss.

The remaining problem is that of loss through evaporation, which is by far the largest and most difficult to overcome, and which has been the subject of a great number of investigations all over the world.

Whenever gasoline is pumped from one container to another, a corresponding quantity of air will escape which unless special precautions are taken, will carry away gasoline vapours varying in amount according to conditions. A rise in temperature will cause the air in a tank to expand and escape, carrying with it a quantity of gasoline corresponding to the degree of saturation and the temperature rise, while by a fall in temperature a corresponding quantity of benzine-free air will again be drawn into the tank, causing another evaporation of benzine. This "breathing" may result in heavy losses.

This is a fact known and recognized by oil engineers, particularly after the fundamental investigations of Wiggins [1] and Ludvig Schmidt.[3]

Wiggins [1] reporting on investigations at the U.S. Bureau of Mines, stated that a considerable part of the leakage was due to equipment such as tanks with leaky roofs and open earthen and concrete containers, and later [2] suggested gas-proof material as the remedy for evaporation loss. The work was continued by Ludvig Schmidt, who, in 1934, published a comprehensive report: "Applied Methods for Reducing Evaporation Losses of Petroleum and Gasoline." [3]

Schmidt stated that through the new methods and improved equipment the total leakage has been reduced by 68 per cent which, in Oklahoma and Kansas, corresponded to over $22,000,000 a year.

He also pointed out the difficulties of ascertaining the exact evaporation loss and mentioned the following method used by the Shell Petroleum Corporation to ascertain the evaporation loss from a 80,000-barrel (approximately 11,000 tons) tank, which clearly proves that it is not a problem for everyone to tackle.

> "The test tank was all steel, with a welded roof, and was equipped with vacuum- and pressure-relief valves operating at one-fourth ounce per square inch. The tank contained crude petroleum having a gravity of 39·2° A.P.I. Recording thermometers gave a continuous record of the vapour and oil-surface temperatures throughout the test period. Accurate measurements were made of the vapour space in the tank, and from the vapour temperature records the breath of the tank due to thermal expansion alone was calculated as amounting to 387,699 cubic feet during the total test period. This volume, however, represents only part of the total volume of the air-vapour mixture expelled, the remainder being due to the change in the vapour pressure of the liquid as a result of temperature changes. A vapour-pressure curve of the crude oil for various temperatures was prepared from which it was determined that only 35 per cent of the total amount of vapour expelled from the tank was caused by thermal expansion of the vapour in the vapour space above the liquid in the tank. Thus the total breath or volume of air–vapour mixture expelled during the test period was determined to be 1,107,711 cubic feet.
>
> "The amount of hydrocarbon vapour in the air–vapour mixture was calculated from the average temperature of the liquid surface and the vapour-pressure curve of the crude oil. For the test period the hydrocarbon vapour represented 40 per cent of the total air–vapour mixture expelled from the tank, or a total of 443,084 cubic feet of gasoline vapour.
>
> "Table 3 gives the Podbielniak analysis of the tank vapours after the air content of the air–vapour mixture had been removed.

" Table 3.—Analysis of hydrocarbon vapours expelled from 80,000-barrel test tank containing crude petroleum.

Hydrocarbon.	Per cent by volume.	Boiling point, °C.	Hydrocarbon.	Per cent by volume.	Boiling point, °C.*
Ethane . .	44·5	—	Butane . .	12·8	+32
Propane . .	25·2	+44	Isopentane .	8·0	+81
Isobutane .	6·5	+11	Pentane . .	3·0	+96

* These boiling points are obviously not °C but seem to be Fahrenheit. Recalculated in °C. the following values are found :

Butane	0° C.
Isopentane . . .	27·2° C.
Pentane	35·5° C.

which gives a closer agreement with the actual values.

" The determination of the number of cubic feet of vapour per gallon of liquid is given in Table 4.

" Table 4.—Calculations giving cubic feet of vapour per gallon of liquid.

Hydrocarbon.	Cubic feet of gas per gallon of liquid.*	Per cent in vapour, see Table 3.
Ethane	46·7	× 44·5 = 20·78
Propane	38·2	× 25·2 = 9·63
Butane	32·5	× 19·3 = 6·27
Pentane	27·3	× 11·0 = 3·01
Vapour per gallon of liquid, cubic feet .		39·69

* Oberfell, G. G., and Alden, R. C. *Natural Gasoline*, Chicago, 1924.

" Since the hydrocarbon vapour lost totalled 443,084 cubic feet and 39·69 cubic feet of this vapour is equal to 1 gallon of liquid the total amount of lighter hydrocarbons lost by evaporation was 11,163 gallons (266 barrels). The evaporation loss for the same test period, determined by careful gauging, amounted to 267·89 barrels, with a change in gravity of 0·105° A.P.I."

Considering the difficulties of correctly measuring quantities and temperatures in big tanks, and coupling this with the fact that the basis of the calculations is scarcely correct, the agreement between the measured and the calculated values can only be explained by a series of simultaneous—almost incredibly fortunate—coincidences.

It will be noted that the method is so complicated and takes up so much time that it is almost useless in practice.

Methods of Analysis.

A study of these investigations clearly indicates the necessity of a reliable and quick method of ascertaining the gasoline vapour content in an air gasoline-vapour mixture.

An electrical method for the determination of small quantities of hydrocarbons in air, in which wires of uniform resistance are caused to glow in air and in the air–vapour mixture under test, were rejected partly as not

being sufficiently accurate over the required vapour concentration ranges and partly on account of the fire risks involved in its use in depots.

After considerable experimental work it was found that an Orsat apparatus using absorbing oils as reagents proved to meet all requirements, *i.e.*,

(1) Parallel analyses gave results which showed sufficient agreement between ascertained and calculated values,
(2) An analysis could be completed in from 10 to 15 minutes,
(3) An operator could soon learn how to manipulate the apparatus.

The Apparatus Used.

For the analysis a 50-ml. Orsat apparatus (Fig. 1) was used. The measuring cylinder was divided into 0·1 ml, corresponding to 0·2 per cent, and readable to 0·05 ml.

The sealing liquid was a strong solution of sodium chloride in water, as hydrocarbons are less soluble in this solution than in pure water—a fact of special importance when dealing with aromatic hydrocarbons.

The apparatus has three ordinary absorbing pipettes filled with glass tubes. The glass tubes give the oil a very large surface, and consequently the pipettes work as quickly as Heinz pipettes, and are easier to manipulate, as bubbles on the surface, which are rather difficult to remove from the viscous oil, can be avoided. Moreover, the double-bore cocks of the Heinz pipettes are a source of constant troubles, whereas the cocks of ordinary pipettes are easily kept in perfect order.

The apparatus was slightly altered to facilitate volume readings and to increase its reliability in use.

Provided that unsuitable absorption liquids do not induce systematic errors, the greatest source of error in the Orsat apparatus lies in the temperature change of the sample from the time of measuring off until the analysis is completed. In analyses with hydrocarbon contents of about 20 per cent a change in temperature of 0·5° C represents a deviation of 0·15 per cent, an error far too high for these analyses.

It is therefore important that a large water-jacket be provided for the measuring tube, and that the working temperature be kept as close to the room temperature as possible.

In order to prevent the heat of the hand being imparted to the sealing liquid, the level bottle is provided with an insulating handle.

The reading was considerably improved by a simple device. It consists of a magnifying glass for taking the final readings. If care is taken that the liquid levels in the level bottle and in the measuring tube are exactly in line, parallax errors may easily be avoided.

Probable Error in the Results of the Analyses.

In the analyses the volume percentage of vapour contained in the air mixture is measured, but to investigate leakages it is necessary to know the number of grams or ml of benzine contained in 1 litre of air mixture.

As the volume of 1 gram molecule of vapour at 0° C and 760 mm Hg is equal to 22·4 litres, an air mixture, the analysis of which shows 22·4 per cent, will contain 1 gram molecule in 100 litres at 0° C and 760 mm. If the molar weight is known the amount of vapour which the air mixture

contains according to the analyses may be calculated either in grams or in millilitres per volume unit.

Vice versa, if the number of grams contained in each litre of air mixture is known, the mean molecular weight of the evaporated material may be calculated. Both methods of calculation have been used in the investigations described here.

Air–vapour mixtures containing a known quantity of a pure hydrocarbon have been used to check the accuracy of the method. For this a known weight, a gm, of pentane is evaporated into b ml of air, measured at a known pressure, p mm, and temperature $t°$ C. At the same pressure and temperature throughout, the mixture so formed is Orsat-analysed, and found to contain say c per cent by volume of hydrocarbon vapour; calculations are as follows, the total volume of the mixture at n.t.p., which need not be directly measured, being called q ml below.

At 0° C and 760 mm the volume of air in the mixture is d ml, where d is given by

$$d = b \,.\, (273/760) \,.\, (p/[273 + t]),$$

and again

$$d = q \,.\, (100 - c)/100,$$

since $(100 - c)$ per cent of the mixture is air, so that q is known from

$$q = 100 \,.\, d/(100 - c).$$

The molecular weight M of the hydrocarbon, the number of grams of its vapour which at 0° C and 760 mm will occupy 22,400 ml, is then calculable from

$$M = 22{,}400 \,.\, a/(q \,.\, c/100).$$

The probable error of the molecular weight will be :

$$\Delta M/M = \sqrt{\{(\Delta a/a)^2 + (\Delta b/b)^2 + (\Delta p/p)^2 + (\Delta t/t)^2 + [100\Delta c/c(100 - c)]^2\}}$$

the weight of a is determined with 0·1 mg accuracy and is around 0·5 grams.

$\Delta a/a$ is consequently 0·0001/0·5 or 0·02 per cent, b is 0·5 to 1 litre, and the probable measuring error may be estimated at 1 ml :

$$\Delta b/b = 1/500 \text{ to } 1/1000 = 0{\cdot}2 \text{ to } 0{\cdot}1 \text{ per cent}$$

the barometer pressure p is read with an accuracy of 0·5 mm,

$$\Delta p/p = 0{\cdot}5/760 = 0{\cdot}07 \text{ per cent}$$

t is read with an accuracy of 0·5°

$$\Delta t/t = 0{\cdot}5/300 = 0{\cdot}2 \text{ per cent.}$$

The probable error in reading the Orsat apparatus is 0·1 per cent and as c lies between 7 and 40 per cent, it will be under the most unfavourable circumstances :

$$(100/93) \,.\, (0{\cdot}1/7) = 1{\cdot}5 \text{ per cent}$$

and under the most favourable circumstances :

$$(100/60) \,.\, (0{\cdot}1/40) = 0{\cdot}4 \text{ per cent.}$$

Consequently—

at its best :

$$\Delta M/M = \sqrt{(0{\cdot}02^2 + 0{\cdot}1^2 + 0{\cdot}07^2 + 0{\cdot}2^2 + 0{\cdot}4^2)} = 0{\cdot}5 \text{ per cent}$$

and at its worst :

$$\Delta M/M = \sqrt{(0{\cdot}02^2 + 0{\cdot}2^2 + 0{\cdot}07^2 + 0{\cdot}2^2 + 1{\cdot}5^2)} = 1{\cdot}5 \text{ per cent.}$$

The measuring tube of the Orsat apparatus used was calibrated by weighing water run out from mark to mark. The greatest discrepancy found was 0·03 ml or 0·06 per cent on the total capacity, which is less than the probable error in reading.

The Absorption Oils.

Both mineral and coal tar oils were used for absorption, the former being mineral colza and Marcol II of the following approximate specifications :

	Mineral Colza.	Marcol II (Bayol. J.).
Gravity, ° A.P.I.	39·8–40·2	34·0–36·0
Flashpoint (P.M. open cup) . .	250° F min	350° F min
Colour, Saybolt	15	Above 30
Viscosity, 100° F.	—	80–90 Saybolt

During the experiments no actual difference in the two oils was found. Marcol II may perhaps work a little faster in the case of small vapour concentrations.

As a result of experiments with aromatic hydrocarbons it became apparent, as mentioned later, that the absorption ability of paraffinic oils towards aromatic compounds is not always reliable. Whenever aromatics were present it was therefore necessary to apply tar distillates like heavy oil and anthracene oil, which, as may be expected, have a high absorption capacity.

An examination of the reaction of anthracene oil towards pentane showed that the absorption of the last part is very slow. An analysis with the anthracene oil as an absorbent showed 23·6 per cent, while Marcol II absorbed another 0·2 per cent up to 23·8 per cent, a result which corresponds exactly with the calculated figure.

From these investigations it is suggested that one pipette be used with heavy oil, one with anthracene oil, and one with mineral colza, Marcol II, or a similar paraffinic oil.

The absorption takes place in the sequence mentioned.

The heavy oil is convenient to work with because of its low viscosity; it works well when the vapour concentration is high, but rather slowly in the case of low vapour concentrations. As the last two pipettes containing respectively anthracene oil and Marcol II are only used for air mixtures with low concentrations, the oils may be used for approximately 100 analyses before a change is necessary.

This procedure guarantees a complete absorption as long as the first pipette (containing heavy oil) will absorb the main part and the absorption in the second pipette (anthracene oil) amounts to only a small percentage.

Should it be necessary to make two analyses simultaneously, one sample can be kept in the heavy oil pipette and absorption of the other sample commenced in the anthracene oil pipette. This procedure has been used in the analyses of tank-car air mixtures mentioned later.

All analyses mentioned in this paper were made in duplicate, and in no case has the difference exceeded 0·1 per cent.

In order to determine whether the sodium chloride solution in the measuring tube would absorb vapour during the measuring, and thereby make the result of the analysis inaccurate, an attempt was made to use mercury as sealing liquid, but the difficulties outweighed the advantages.

The object of the first experiments was to ascertain the relative accuracy of the method. Some fifty analyses of gasoline-vapour/air mixtures were made as in duplicate or triplicate, and the results showed a maximum deviation of 0·2 per cent.

The Applicability of the Analytical Method.

(1) *Aliphatic Compounds.*

The congruity of the parallel tests does not prove the applicability of the method, and it was therefore necessary to supplement the first experiments

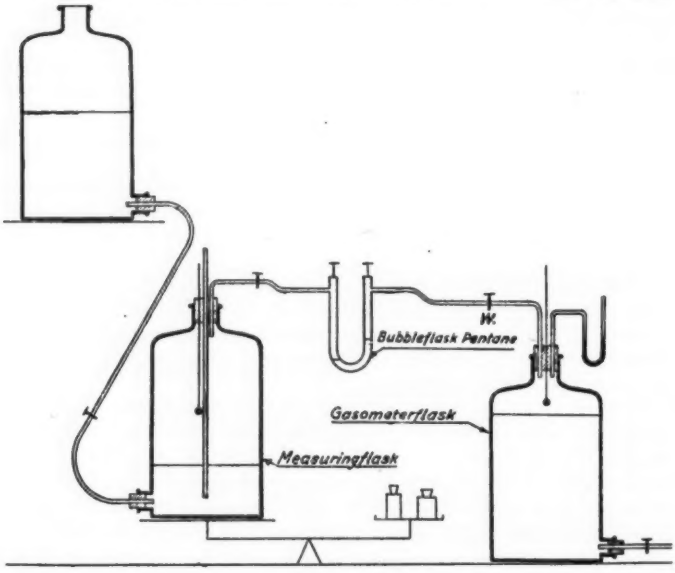

Fig. 2.

by investigations as to their absolute accuracy. For this purpose pentane/air mixtures of known pentane content were Orsat-analysed, and the molecular weight of the pentane calculated.

From a weighed measuring bottle with discharge pipe, thermometer, and

manometer, air is forced by water pressure through a bubble flask containing the pentane and into a gasometer bottle.

The quantity of air was ascertained to an accuracy of 1 g by weighing the amount of water which has replaced the air. The submerged glass tube manometer allowed the pressure to be estimated to an accuracy of 1 mm water column and the pentane charge in the measured air volume was ascertained by weighing the bubble flask before and after the test.

For the first experiments a gasometer bottle with water sealing and bubble bottle with glass cocks (Fig. 2) was used, but it was impossible to keep the glass cocks tight, and pentane vapour was undoubtedly lost during the weighing. Moreover, the first experiments show a systematic error as shown in Table I.

TABLE I.

Pentane I Fraction from Petroleum.

Orsat percentage measured.	Molar weight, calculated.	Molar weight for pentane.
19	78·4	72
25	77·3	—
30·5	77·0	—
35·0	76·4	—

The degree to which pentane dissolves in water, which in " Landolt-Börnstein " is given as 0·035 g/100 ml at 17°, is of some importance in this instance, and the low percentage contents give the greatest error.

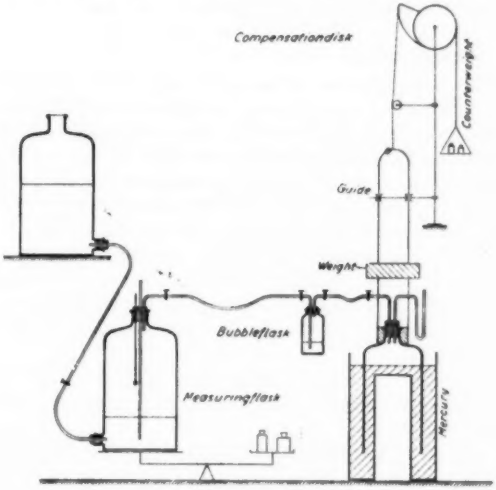

FIG. 3.

The method of experiment was therefore changed, a bubble bottle with rubber hose and pinch-cocks being used instead of glass cocks. The tightness was examined several times by weighing after a period of 10 to 15

minutes. In spite of the heavy pressure caused by heating the pentane to room temperature after the evaporation, the loss never exceeded 0·0005 g.

The gasometer was reconstructed to use mercury as the sealing liquid. The mercury was placed in an iron container, and the gasometer consisted of a bottomless glass bottle, to the neck of which was affixed a "hairpin" of 6-mm iron wire guiding the gasometer bell suitably counterpoised as shown in Figs. 3 and 4.

After trials on an impure pentane fraction from petroleum, the following satisfactory results were obtained on a sample of synthetic *n*-pentane, whose molar weight could be relied on to be 72 :

TABLE II.

Synthetic n-*Pentane.*

Quantity evaporated, g.	Orsat percentage.		Molar weight calculated.	Absorption oil.
	Measured.	Calculated.		
0·5877	18·35	18·34	71·9	Marcol II.
0·5678	16·0	16·05	72·3	,,
0·9186	23·8	23·8	72·0	Heavy oil, anthracene oil and Marcol II.
	7·5	7·49	71·9	

The variations of the percentage figures found are so small—0·4/72 = 0·5 per cent—that it may be taken as proof that the analysis shows the correct values, as the results are within the limits fixed for the probable error, and the absorption in the oils is complete.

(2) *Aromatic Compounds.*

Analyses using pure benzene of molar weight 78·05 showed percentage values too low, and consequently molar weights too high. Using Marcol II and mineral colza, molar weights of 178 were obtained and when tar oils were used as the absorption liquid a molar weight of 141 was obtained. It was certain that no errors could be due to changes of temperatures.

In the formula for the calculation of the molar weight the Orsat percentage appears twice, once directly and once as a factor of q.

An attempt was therefore made to measure directly the item $100 \cdot d/(100 - c)$, *i.e.*, the volume of the vapour/air mixture together with the measurement of c. It would thereby be possible to control the source of error, whether it was due to the method of analysis or to the forming of the vapour/air mixture.

At known temperature and pressure exactly 100 ml air were passed through a weighed benzene bubble bottle to a 100 ml mercury-sealed measuring tube (Fig. 5).

By evaporation of 0·0276 g benzene in 100 ml air (20·5°, 745 mm) a total volume of 104·65 ml was measured. As 78·05 g benzene at 0° and 760 mm should equal 22·4 litres, 0·0276 should equal $22{\cdot}4 \cdot 0{\cdot}0276/78{\cdot}05 = 7{\cdot}92$ ml or at 20·5 and 745 mm, 8·68 ml against the 4·65 found.

The apparent molar weight would therefore be :

$$78 \cdot 8{\cdot}68/4{\cdot}65 = 146.$$

The analysis showed 4·4 per cent and accordingly the molar weight

$$= 0{\cdot}0276 \,.\, 22{\cdot}4 \,.\, 1000/4{\cdot}4 \,.\, 104{\cdot}65\ (273/760)\ (745/293{\cdot}5) = 147.$$

This may be explained by the assumption that either the benzene molecules are associated at low temperatures or an adsorption of the benzene to the glass and the mercury surface takes place.

Only one analysis of the mixture was made, the results being given in Table III.

TABLE III.

Benzene Determination.

Quantity evaporated, g.	Orsat percentage.	Molar weight.	Remarks.
0·3500	4·5	178	Marcol II.
0·3630	5·9	142	Anthracene oil.
0·0276	4·4	147	Heavy oil.
0·0276 in 100 ml air	4·44	144	Volume increase measured directly.
0·3638	6·3	129·5	Gasometer and measuring tube "flushed."

In order to verify the theory of adsorption two consecutive mixtures were made in the gasometer, as it is possible that the glass and the mercury surface would become saturated with the first mixture, and make it possible to keep the other mixture intact.

The measuring pipe of the Orsat apparatus was "flushed" with mixture, and the analysis showed 6·3 per cent and the molar weight 129·5. It can hardly be expected that the "flushing" should leave the absorbed benzene unaffected, as the mercury in the gasometer and the water in the measuring pipe cover the glass surfaces, thereby renewing their own surfaces, but there is a marked decrease in the molar weight, and there is little doubt that there is an adsorption phenomenon.

As the aliphatic compounds have shown no adsorption phenomenon, it was decided to investigate whether a dilution with pentane would have any influence on the benzene. The molar weight was determined for three mixtures of benzene and pentane (Table IV).

TABLE IV.

Benzene–Pentane Mixture.

Per cent. benzene.	Molar weight.
10	73·7
20	75·3
50	81·8

Only the last molar weight is abnormally high.

These experiments show that there are no difficulties when the benzene vapour is diluted with other hydrocarbons, and that the method may therefore be applied to all qualities of gasoline, even if they contain rather large quantities of benzene.

From the investigations described below it appears that the assumption that the molar weight of the evaporated fraction is about 70 will not be far

wrong. As the specific gravity is very close to 0·7, a gasoline–vapour/air mixture showing an Orsat analysis of 22·4 per cent will contain 1 litre or 0·7 kg benzine per cu m at 0° C and 760 mm pressure.

Determination of Molar Weight.

The use of pentane for controlling the Orsat values proved that the accuracy of the method was sufficient to show a close agreement between the measured values and the percentage values calculated on basis of the molar weight. The analysis may therefore be used for the determination of the average molar weight of volatile fractions, as was the case, for instance, with the pentane.

The methods so far used in the petroleum industry [4] are the cryoscopic and the ebullioscopic method, with different solvents for higher-boiling fractions and pure components, and the vapour-density method for gases. These methods, although giving very good results for pure compounds, may fail when applied to mixed fractions on account of the influence of unknown factors. If, for instance, part of the solvent is contained in the mixture, the results may be quite wrong, and in the same way the results will be influenced by the " molar association "—a term used here to cover processes causing the solution not to follow the rules of ideal solutions. Moreover, it is more difficult to work with a solution of volatile fractions, as it is often quite impossible to control the changes of its concentrations.

It is obvious that no direct proof can be given of the applicability of the Orsat method to the determination of the mean molecular weight of, for instance, a gasoline fraction.

However, a series of experiments may be carried out under conditions varied, so that a comparison of the results will be warrantable.

By the apparatus (Figs. 3 and 4) used in the experiment the mean molar weight of the evaporated gasoline fraction may be found, and if the same sample is used for consecutive experiments, a series of molar weights will be found for the evaporated fractions. On the basis of these figures the molar weights which would have been obtained may be computed, if each experiment was made with a new quantity of gasoline, but with the corresponding evaporated percentage. If these values are put down graphically, they will form a curve, which will illustrate the variation of the mean molar weights of the evaporated quantities.

This curve may be verified by determining the mean molar weight of a certain fraction of the same benzine and changing the percentage evaporated. The molar weights determined must then comply with the curve, if both the curve and the molar weights are correct.

For serial tests the constancy of the temperature is very important, and, as previously mentioned, the level flask was provided with an insulated handle, and the temperature of the room was kept so constant that the variation in the temperature of the water-jacket did not exceed 0·2° C.

The tests were carried out with 40 g benzine weighed in a bubble flask, and the same sample of benzine was used for all the experiments. The molar weights Mf_n found therefore constitute the mean molar weight of the fraction evaporated between the two percentage quantities, and were converted into the molar weight Mo_n of the total percentage evaporated.

TABLE V.

n.	Molar weight.	
	Mf_n found.	Mo_n converted.
1	67·65	67·65
2	71·0	69·1
3	73·1	70·6
4	74·1	71·4
5	76·0	73·0
6	78·8	74·0
7	80·0	74·8
8	81·3	75·6
9	82·9	76·3
10	83·5	76·6

In Fig. 6 the converted molar weights are indicated by + on the full curve. The " limit " molar weight was determined as 65·9 by evaporation of 0·7 per cent.

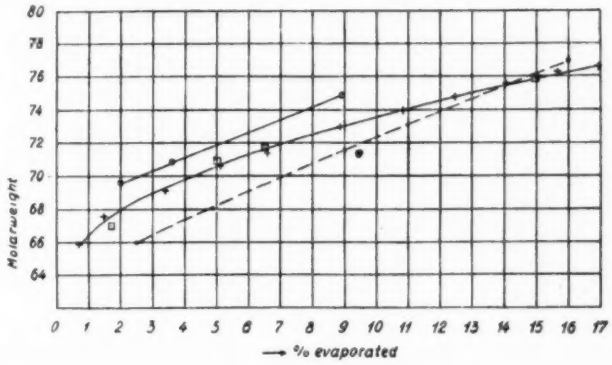

FIG. 6.

The molar weight of the same gasoline was determined for four fractions, but each time with different quantities weighed and evaporated.

TABLE VI.

Weighed quantity, g.	Evaporated, per cent.	Molar weight.	
		Found.	According to curve, Fig. 6.
24·52	1·7	67	67·6
21·53	4·97	70·9	70·60
10·40	6·5	71·7	71·7
4·27	14·9	75·9	76·05

The molar weights found are indicated in Fig. 6 by ⊡.

The agreement between values found by different methods were fully satisfactory, although it must be borne in mind that—as shown by the benzene results—the method gives the molar weight of the material as a vapour and not as a liquid.

The Reid vapour pressure of the gasoline used for the experiments was rather high—10·5 lb at 100° F, and it is therefore likely that it contained small quantities of propane and butane, an assumption which agrees with its low " molar weight limit " and the rather big increase of the molar weight during the first part of the curve.

The gasoline was Engler distilled, and half of the total distillate was again Engler distilled, the balance being used for the determination of the molar weight.

The fact that the butane and propane contents only appear as losses causes a corresponding increase of the mean molar weight to be shown by the molar weight determination. This might very well be expected considering that the two hydrocarbons will boil at respectively −0·1° and −44° C, and that no great condensation will therefore take place in the Engler apparatus.

Engler Distillation (see Fig. 7).

	Engler I.	Engler II.
I.B.P.	38° C.	38° C.
	Per cent.	Per cent.
50° C.	5·0	4·0
60	11·5	10·5
70	19·0	18·5
80	27	27
90	35	35
100	43	43
110	51	51
120	58·5	59·5
130	65·5	66·5
140	73	74
150	80	80·5
160	85	87
170	90	91·5
180	94	94·5
190	96	96·5
F.B.P.	196° C.	191° C.
	Per cent.	Per cent.
Total distillate	97	97
Loss	2	2
In flask	1	1
	100	100

The converted molar weight of the Engler distillate is indicated in Fig. 6 by O.

From the vapour pressure equations :

$$lnp = -L/RT + C$$

in which L is the molar evaporation-heat, it appears that the vapour pressure rises rapidly with increasing temperatures, and as the molar evapora-

TABLE VII.

The Molar Weight Variation of the Engler Distillate.

Evaporated, per cent.	Molar weight.		According to curve for gasoline, Fig. 6.
	Found.	Converted.	
2	69·6	69·6	68·0
3·6	72·3	70·8	69·6
8·9	77·8	74·9	73·1

tion-heat divided by the boiling-point temperature is almost constant and the boiling point rises considerably when the molar weight is increased, it will be seen that the lower the molar weight the higher will be the rise of the vapour pressure at a certain increase in temperature. In the case of heating —as during Engler analysis—the vapour pressure increase will therefore mostly be due to hydrocarbons of low molar weights, which are more plentiful in the distillate than in the case of air-current evaporation. The above will likewise appear quite clearly from the molar weight determination of the Engler fractions.

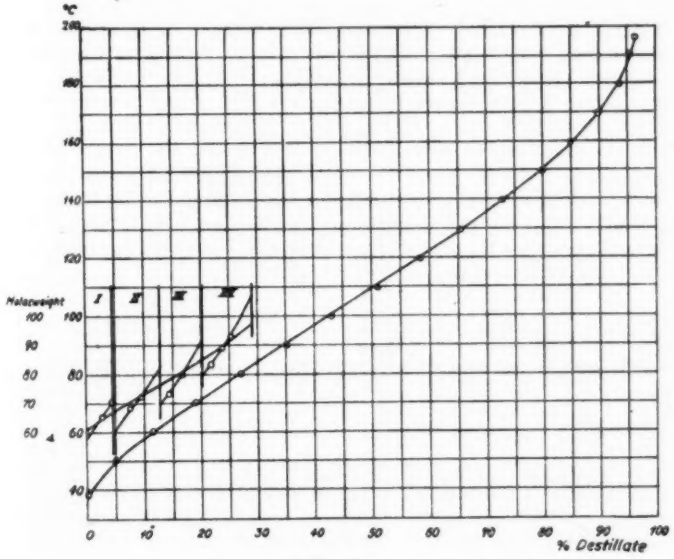

FIG. 7.

The volume percentage distilled in an Engler distillation cannot be measured with reasonable accuracy, and errors are cumulative. The results were therefore outlined graphically and the measured values of the distilled quantities were corrected by means of the normal Engler curve, Fig. 7.

TABLE VIII.

Engler Distillate of Gasoline.

	Fraction.	Final temperature ° C.	Corrected fraction according to the Engler curve converted into weight, per cent.	Evaporated, per cent.	Molar weight converted.
	I.B.P.	35			
I	5 per cent.	51	4·55	2·5	64·7
				4·5	70
II	12·5 „	65	12·99	7·51	68·0
				9·16	71·7
III	20 „	75	20·27	14·39	73·4
				15·06	77·3
				16·63	79·8
IV	30 „	87	29·26	22·1	83·8
				24·96	88·3
				25·27	92·4

On Fig. 7 the converted molar weights from Table VIII are plotted against the percentage evaporated giving the molar weight curve for each fraction.

The mean molar weight of each fraction would be represented by the central points falling on an even curve. The molar weights of these fractions are recalculated to represent the mean molar weight of the total quantity evaporated, as previously mentioned, and the values found are plotted on the same figure as the original molar weight curve (dotted on Fig. 6); it will be seen, as might be expected, that the fractionation by Engler distillation shows a steeper curve with a lower initial molar weight.

These experiments all tend to show the applicability of the Orsat method to the determination of mean molar weights.

EXAMPLES OF THE APPLICATION OF THE METHOD OF ANALYSIS.

The importance of the speed of the Orsat method is soon realized in practice.

Filling of Tank Cars.

In investigating the effect of top and bottom filling of tank cars, two rail tank cars, each of 15 cu m and of uniform construction, were filled with gasoline from the same tank. They were filled in 70 minutes through a 3-inch pipe, one from the top and one from the bottom. Both had previously carried gasoline discharged four days before.

Analyses were made of the air contained in the tank previous to the filling and of the air escaping when a quarter, half, three-quarters and wholly filled.

During filling through the open dome, this was covered by a close-fitting cardboard lid to eliminate wind effects. The results of the Orsat analyses were :

FIG. 1.

[*To face p.* 541.

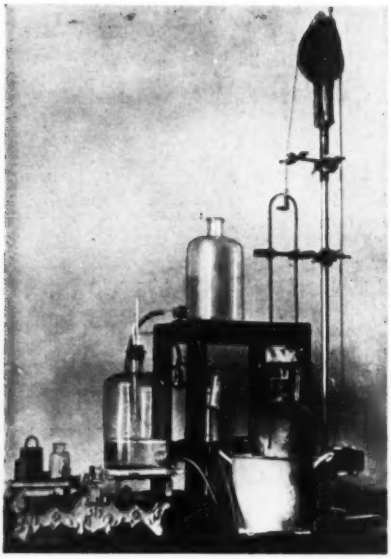

FIG. 4.

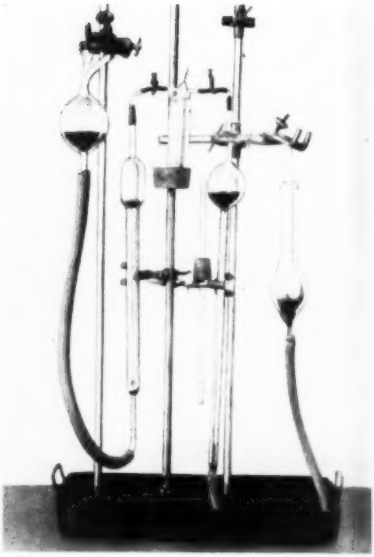

FIG. 5.

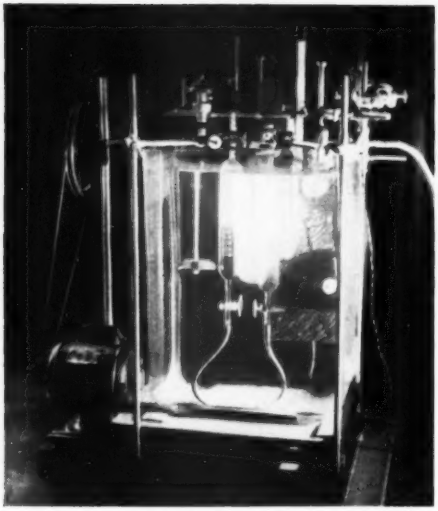

FIG. 9.

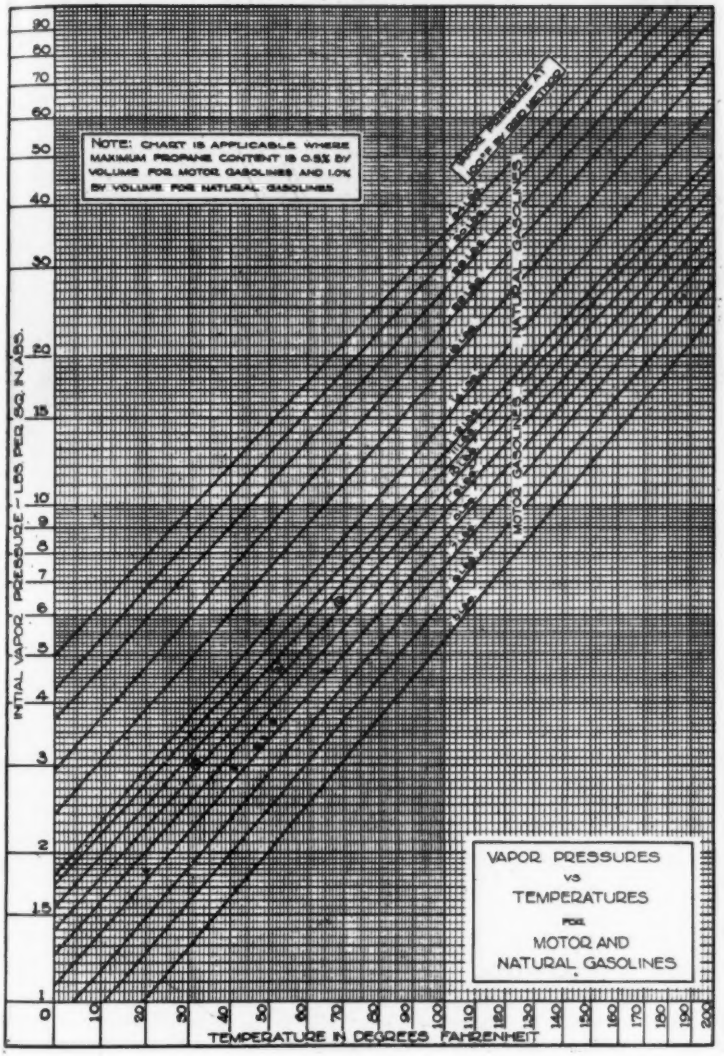
NOTE: CHART IS APPLICABLE WHERE MAXIMUM PROPANE CONTENT IS 0.5% BY VOLUME FOR MOTOR GASOLINES AND 1.0% BY VOLUME FOR NATURAL GASOLINES
INITIAL VAPOR PRESSURE - LBS PER SQ. IN. ABS.
TEMPERATURE IN DEGREES FAHRENHEIT
VAPOR PRESSURES vs TEMPERATURES FOR MOTOR AND NATURAL GASOLINES

FIG. 10.

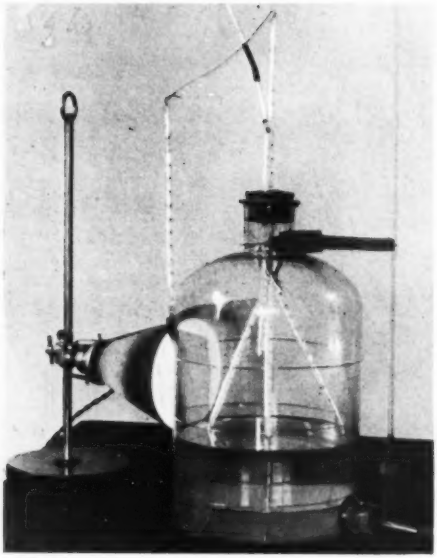

FIG. 13.

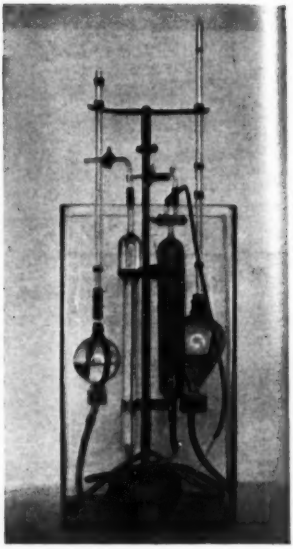

FIG. 22.

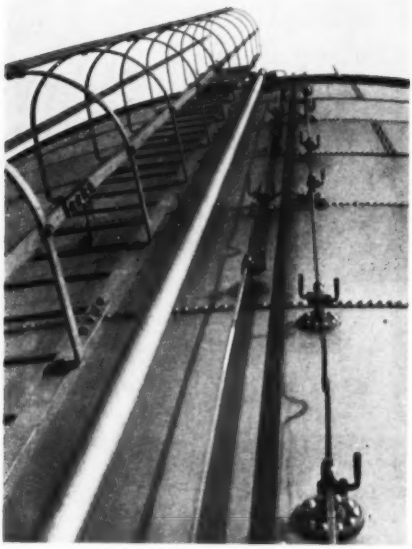

FIG. 24.

TABLE IX.

	Under-surface loading.		Splash loading.	
	Per cent lost.	Increase.	Per cent lost.	Increase
Empty car	3·4	—	3·2	—
1/4	3·4	0	18·0	14·8
1/2	3·4	0	21·8	18·6
3/4	5·0	1·6	25·4	22·2
1/1	21·0	17·6	23·6	20·4

Atmospheric temperature was 9° C; the weather overcast.

If the air-mixture percentages are plotted against the filling degree (Fig. 8), it will be noted that by the splash loading 50 per cent of the

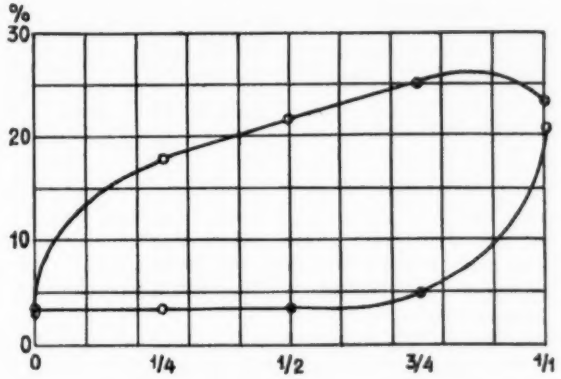

FIG. 8.

escaping air will be supersaturated, as the saturation percentage of this gasoline at 9° C is 21·2. Part of the gasoline is consequently lost in its unevaporated form, but the droplets are so small that they cannot be directly observed. However, if the air outlet is comparatively small an object held in the discharged air will be moistened with gasoline.

This is not a new or epoch-making discovery, but it has supplied satisfactory information on the mechanism of a well-known phenomenon and shows that the Orsat method is excellent for investigation of losses.

The Saturation Percentage.

The saturation percentage of benzine–air mixtures at various temperatures was determined for two different gasolines (*a*) in a 300-litre test tank containing approximately 100 l gasoline, and (*b*) in a thermostatically-controlled laboratory apparatus holding approximately 300 ml gasoline (Fig. 9).

TABLE X.

Gasoline a in 300-Litre Test Tank.

Temperature.		Saturation percentage.	Vapour pressure calc., lb.
° C.	° F.		
−6·5	20	12·5	1·84
+5·0	41	20·2	2·97
8·5	47	22·0	3·23
9·5	49	22·6	3·32
10·6	51	25·0	3·68
18·0	64·4	31·5	4·63

TABLE XI.

Gasoline b in Laboratory Apparatus.

Temperature.		Saturation percentage.	Vapour pressure calc., lb.
° C.	° F.		
0	32	20·4	3·00
11·2	52	32·2	4·73
21·0	69·8	42·0	6·17

The two gasolines originally had a Reid vapour pressure of 8·5 and 11·7 lb respectively at 100° F.

It will be noted that the calculated values correspond closely with the Brown vapour pressure curve for the " 8·5 gasoline," while the curve for the " 11·7 gasoline " corresponds to the calculated values of a " 10·5 gasoline," as shown in Fig. 10.

Considering that a Reid vapour pressure of 11·7 is always due to the addition of very small quantities (0·25 to 0·5 per cent) of highly volatile compounds, it is quite likely that when the sample finally reached the container in the thermostat after several transfers it had a Reid vapour pressure of 10·5 only.

In case of the " 8·5 gasoline " it appeared that the test tank value, with the comparatively large quantity of gasoline filled direct from the main tank of the plant, was higher than the corresponding laboratory values, where the gasoline was transferred at least twice.

There can be little doubt, however, that the Brown vapour-pressure curves may very well be used for determining the saturation percentage of the different gasolines.

THE BREATHING LOSS.

An approximate formula for breathing loss, adjusted for the effect of concurrent change in fluid gasoline content of the tank, may be deduced from Boyle–Mariotte's law. If in the period considered :

t is the rise in temperature of the tank air,
p_1 is the pressure at which the relief valve operate inwards,

δp is the pressure increase from inward to outward operation of the relief valves,

V_1 is the air volume in the tank before oil is pumped into it,

v is the volume of oil pumped in, so that

$V_2 = V_1 - v$ is the air volume in the tank after pumping in, while

$\delta\pi = \pi_2 - \pi_1$ is the rise in vapour pressure of the gasoline caused by that increase in its surface temperature which corresponds to t,

then if v is pumped in, the pressure will change to p_2, where

$$p_1 \cdot V_1 = p_2 \cdot V_2 \text{ or } p_2 = p_1(V_1/V_2).$$

If the tank air is heated through $t°$ C, the pressure will change to p_3, given by

$$p_3 = p_2(273 + t)/273 = p_2(1 + t/273).$$

If the gasoline vapour pressure rises by $\delta\pi$, the pressure changes to p_4, given by

$$p_4 = p_3 + \delta\pi.$$

If the tank relief valves operate outwards at a pressure $p_1 + \delta p$, the volume L of vapour lost, measured at this pressure, will be approximately

$$L = V_2 \cdot p_4 - V_2(p_1 + \delta p)$$

which on substitution and reduction leads to

$$L = V_2 \cdot p_1[(V_1/V_2)(1 + t/273) + \delta\pi/p_1 - \delta p/p_1 - 1)].$$

The formula also applies when oil is delivered from the tank; here v is taken as negative, so that $V_2 > V_1$.

If the gasoline content of the tank does not alter, then $V_2 = V_1 = V$ say, and

$$L = V \cdot p_1(t/273 + \delta\pi/p_1 - \delta p/p_1)$$

a formula which is in general use for the breathing loss from a standing tank.

Under American conditions [7] the rise in temperature of tank air is about $1\frac{1}{4}$ times the rise in the atmospheric temperature from night to day, and the variation in the temperature of the gasoline surface may be estimated at about 10° C at maximum.

The formulæ just given are approximate only, and a method of improving them is discussed below.

Various analyses of the air contained in large tanks show that its degree of saturation decreases with the distance from the gasoline surface. Table XII illustrates this.

TABLE XII.

Test No.	1.			2.	
Height above surface, m	0·5	5·0	9·5	0·4	4·5
Atmospheric temperature, ° C.	7	7	8	9	10
Orsat, per cent	17·6	16	15	24·6	23·5
Saturation, per cent		17·8		24·6	

These analyses were all made at increasing tank temperature and pressure in cloudy weather and show results of importance in calculating evaporation

loss. They warrant further investigation. While diffusion of the gasoline vapours in the tank air is of importance, it is not the controlling factor, as air-currents will always arise in the air space of a tank, particularly during discharge.

Temperature differences due to the sun and to heat radiation also produce air currents which tend to equalize differences in vapour concentrations, so that the upper layer will contain more benzine vapours than would be the case if only diffusion was of importance.

Diffusion.

In order to examine the diffusion and to exclude all possibilities of air currents, a laboratory "tank," approximately 3·5 m high and 77 mm diameter, was constructed. As the plate thickness of the tube was approximately 5 mm, and the room temperature was kept constant at 20° C±1° C, it may be assumed that there was no unilateral heating with consequent air currents. Along a generatrix 10-mm holes were drilled at each 25 cm and closed with cork stoppers. The top of the tank was covered by a loosely attached cap in order to protect it against currents in the surrounding air. Through the lower hole—*i.e.*, 25 cm above the bottom—1 litre gasoline was carefully poured into the tank by means of a rubber tube leading to the bottom.

The gasoline had a Reid vapour pressure of about 8·5 lb at 100° F, and at 20° C showed a saturation percentage of 29·0 Orsat.

Air samples for the analyses were taken through the holes in the tank wall by means of a glass pipe connected with the suction pipe of the Orsat apparatus, the sampling commencing from the top in order not to disturb the air column below. 1-litre gasoline equals a height of 21·5 cm in the tank, and consequently the distance from the surface to the first hole is 53· cm.

Table XIII and the curves (Fig. 11) show the results of the experiments.

TABLE XIII.

Hole No.	Orsat, per cent.			
	1½ hours.	18 hours.	66 hours.	240 hours.
1	27·6	29·0	28·2	25·6
2	13·8	24·9	26·0	24·0
3	3·6	20·8	23·6	22·7
4	0·5	16·9	21·2	—
5	0·0	13·0	18·6	18·4
6	0·0	9·6	16·2	16·3
7	—	6·8	13·9	14·3
8	—	4·5	11·7	12·2
9	—	2·8	9·6	10·1
10	—	1·2	7·7	8·1
11	—	0·2	5·6	5·9
12	—	0·0	3·8	4·4

These experiments clearly show that the diffusion is of little importance in relation to the vapour distribution in big tanks, as after a period of 18

hours the air in the test tank was not even saturated at a distance of only 30 cm above the surface.

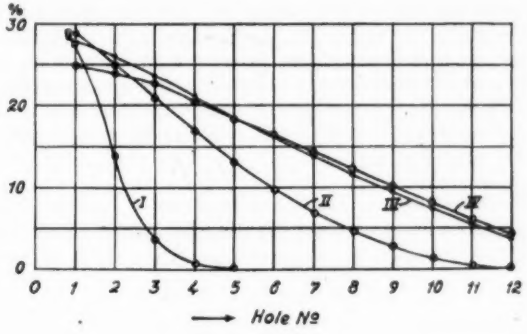

FIG. 11.

If by means of the figures available the diffusion coefficient D is calculated from the formula $dn = -D \cdot q \cdot (dc/dx) \cdot dt$, in which dn is the substance which during the period dt covers the distance dx of the cross section q at a concentration difference of dc, the figures in the first two columns will show

$$D_1 = 0{\cdot}93 \text{ per hour}$$
$$D_2 = 0{\cdot}96 \text{ per hour.}$$

As the concentration at the cross section nearest the gasoline surface after the first 18 hours is no longer constant, the diffusion coefficient of the two last columns was not calculated.

It will be noted that the vapour concentration directly above the surface (at hole No. 1) reaches a maximum in 18 hours.

The analyses made at 66 and 240 hours show an unmistakable decrease, which is explained by the complete evaporation of the volatile compounds by this time. These results are in agreement with the investigations of the saturation percentages, and show how important the volatile bodies are in the storing of gasoline.

Correction of the Theoretical Loss.

In developing the formulæ on page 547 above, it is assumed that all the air in the tank is at once saturated with gasoline vapours at the prevailing temperature. The analyses given show that this is approximate only; the expression for p_4 may then be rewritten as

$$p_4 = p_1(1 + t/273) + k \cdot \delta\pi$$

introducing a factor k to allow for the fact that all the air is not so saturated, and on the further assumptions that there is no change in the air volume in the tank, and that relief valves do not operate. Given the vapour-pressure curve for the gasoline in the tank, k may be calculated in any particular case if the tank air pressure and temperature, and the temperature of the gasoline surface, are also measured or known.

The correction factor is not a constant applicable in all circumstances, as it expresses the difference between the actual and the theoretical vapour concentration in the tank air, and therefore is dependent on how quickly the temperature has risen, on the difference in the temperature of the cold and the warm side of the tank—*i.e.*, the air currents in the tank air—on the height of the air space above the gasoline surface, and on the vapour concentrations at different heights prior to the rise in temperature.

In order to ascertain if the correction factor could be applied to ordinary calculations, two series of experiments were made, one in the laboratory and one in an ocean installation.

Laboratory Experiments.

For the laboratory experiments the arrangement shown in Figs. 12 and 13 was used. Six thermometers were placed in a 10-litre bottle, two in

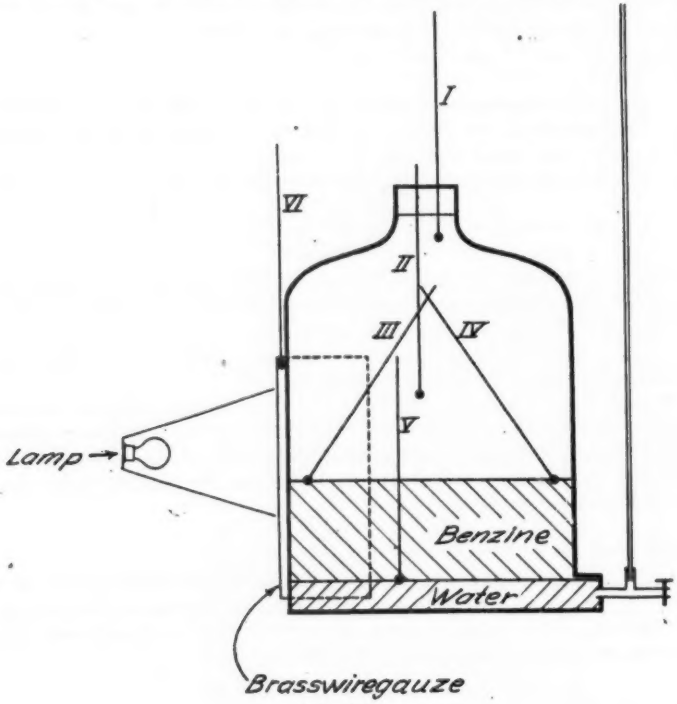

FIG. 12.

the air space above the gasoline, two in the gasoline surface, one in the dividing line between water and gasoline and one outside the bottle.

Half of the bottle was covered by a brass wire gauze, heated by a shaded electric lamp, the object of the gauze being partly to distribute the heat and partly to protect the thermometers against direct heat radiation. The

gasoline was syphoned into the bottle above a layer of water to enable the pressure to be measured directly by the water column. The conditions obtained by this arrangement should be as close as possible to those encountered in practice, although they can never be exactly the same, as not only the relative, but also the actual quantities are of importance. The air space in the bottle will become homogeneous much more quickly than the air space in a large tank. Another drawback of the laboratory experiment is that the sides of a glass bottle do not have the same thermal conductivity as those of a steel tank, although this may be counteracted somewhat by using the gauze.

The unilateral heat of the electrical lamp has a fair resemblance to the heat obtained by regular tanks from the sun.

In order to ascertain if the temperatures measured in the air showed the average temperature with reasonable accuracy—the accuracy of the correction factor k is dependent on the accuracy of the temperatures measured—blank experiments were made with water.

Tables XIV and XV show the results of the two series of experiments.

TABLE XIV.

n.	1.	2.	3.	4.	5.	6.
p_a water	20	60	115	160	200	230
p_a Hg	1·5	4·6	8·8	12·2	15·2	17·5
Temperature, ° C.:						
t_1	22·4	23·1	24·3	25·5	26·8	28·1
t_2	22·0	22·7	23·9	25·0	26·1	27·0
t mean	22·2	22·9	24·1	25·3	26·5	27·6
t calculated	—	23·5	24·9	26·1	27·3	28·4

TABLE XV.

n.	1.	2.	3.	4.	5.
p_a water	88	160	210	270	310
p_a Hg	6·7	12·0	16·0	20·5	23·6
Temperature, ° C.:					
t_1	21·6	22·7	24·4	26·1	27·2
t_2	21·6	22·4	24·2	25·1	26·6
t mean	21·6	22·6	24·3	25·5	26·8
t calculated	—	23·1	25·1	26·4	27·6

If the results are plotted graphically (Fig. 14), it will be seen that the measured temperatures are 0·8° C below those calculated. This difference, which appears immediately at the first measuring, tends to indicate that a heating, which is not registered, takes place along the side heated by the lamp. As both series of experiments were executed under the same conditions as the gasoline experiments, and as the temperature intervals are almost the same, the deviation found may be entered as the correction.

The test tank was made ready for an experiment in the afternoon, and was set aside until next morning without shaking or temperature change,

which might further the equalization of the gasoline vapour concentration in the air space.

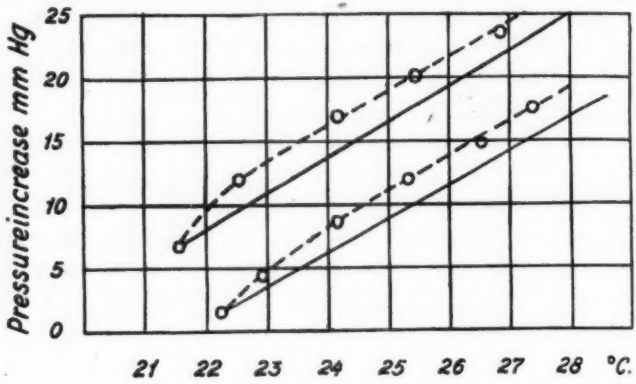

FIG. 14.

During the tank-experiments the corresponding pressures and temperatures were read at suitable intervals, and the correction factor k was calculated on the basis of the corresponding data.

The vapour pressures of the gasoline at the surface temperatures measured were determined on the basis of the previously mentioned vapour-pressure graphs, and by analysing the percentage contents at a known temperature the quality of gasoline used was determined.

At 18·9° C (66° F) the gasoline showed a saturation value of 34·2 per cent corresponding to the 8·7 lb Reid vapour pressure curve.

Tables XVI, XVII, and XVIII show the measured values of three tests carried out on consecutive days.

TABLE XVI.

n.	1.	2.	3.	4.	5.	6.	7.	8.
Time . .	10.00	10.45	11.00	12.00	13.00	14.00	15.30	15.45
p_a, mm water .	69	686	765	975	1080	1140	605	395
Thermo- I .	19·1	24·6	25·8	26·9	27·0	27·5	22·1	20·1
meter II .	19·1	24·0	25·5	26·1	26·3	26·5	21·5	19·8
III .	19·0	22·1	22·6	23·7	24·2	24·6	22·3	21·2
IV .	19·0	22·2	22·6	23·6	24·2	24·6	22·3	21·2
V .	19·0	19·1	19·3	19·5	19·9	20·2	20·7	20·6
VI .	19·2	42	42·5	42·8	43	43	20·7	19·0
k calculated .	—	0·86	0·80	0·93	0·95	0·95	1·07	1·07

The lamp was lighted at 10.00 hours and was extinguished at 14.00 hours.

The experiments of Table XVI and XVII were made in the apparatus shown in Figs. 12 and 13. The thermometers used for measuring the gasoline surface temperature were almost vertical, thus indicating the average temperature of a rather thick layer of gasoline. Endeavours were

TABLE XVII.

n.	1.	2.	3.	4.	5.	6.	7.
Time . .	8.30	8.45	9.00	9.30	10.30	11.45	13.45
p_a, mm water .	—50	233	435	645	830	920	195
Thermo- I .	18·4	21·8	24·8	25·9	26·7	27·2	20·5
meter II .	18·2	21·6	24·1	25·2	25·8	26·2	20·2
III .	18·4	19·7	20·7	22·0	23·4	23·8	20·4
IV .	18·4	19·8	20·8	22·1	23·3	23·8	20·4
V .	18·4	18·5	18·6	18·6	19·1	19·4	20·0
VI .	18·4	34·2	37·5	38	38	38	20·2
k calculated .	—	0·72	0·72	0·77	0·85	0·88	1·35

The lamp was lighted at 8.30 hours and was extinguished at 11.45 hours.

made in the following test series (Table XVIII) to measure the surface temperature more exactly by means of a horizontal thermometer floating on two corks, so that the mercury bulb was just covered by the gasoline. In Table XVIII this thermometer is numbered V, while VI is the bottom thermometer, and the outside thermometer has been dispensed with. The high pressure under which experiments 1 and 2 were executed cannot be obtained in practice, as the pressure valve of regular tanks will lift at a water column of approximately 250 mm, and it is therefore difficult to verify the experiments. By removing the lamp a little from the wire gauze the heating becomes slower, and there will thus be time for a number of measurements within the pressure-interval which may be encountered in practice.

Experiment 3 (Table XVIII) was made with the gasoline stored in the installation tank used for the practical tests. The vapour-pressure curve was determined by carefully syphoning the gasoline into the bottle, which already contained a gasoline-vapour/air mixture, by heating the bottle to approximately 1000 mm water-column pressure, and by setting it aside for about 24 hours for temperature equalization. As the gasoline was filled into the bottle at a rather low temperature, there was a pressure of approximately 150 mm water column, after a uniform temperature had been obtained. The Orsat percentage could therefore be determined directly from the bottle without risk of vacuum.

TABLE XVIII.

n.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Time .	10.00	10.10	10.20	10.32	10.43	10.55	11.08	11.20	13.00	13.30
p_a, mm water .	0	60	110	160	210	260	310	360	310	230
Thermo- I	18·7	19·0	19·4	20·1	20·7	21·5	22·0	22·5	21·0	19·0
meter II	18·7	19·1	19·6	20·1	20·6	21·1	21·6	21·1	20·5	19·6
III	18·7	19·0	19·3	19·6	19·7	20·0	20·3	20·6	20·1	19·7
IV	18·7	18·8	19·1	19·4	19·6	19·9	20·3	20·5	20·1	19·6
V	18·7	19·1	19·4	19·6	19·8	20·2	20·3	20·7	20·1	19·7
VI	18·6	18·6	18·7	18·7	18·7	18·8	18·8	18·9	18·9	18·9
k calc. .	—	0·51	0·46	0·51	0·57	0·55	0·52	0·55	1·04	1·62

The lamp was extinguished at 11.30 hours.

The analysis showed the saturation 40·0 per cent at 65·5° F, corresponding to the 10 lb Reid vapour pressure curve.

As will be seen from the tables, k is almost constant during the last test-series, and within the pressure increase encountered in practice the value is approximately 0·5–0·6. The lower value of k in the last series as compared with that of the two preceding tests is due to the fact that the surface temperature measured for the first two series was too low.

By the fall in temperature when the lamp is extinguished the k value will rise above 1·0, as the gasoline quantity contained in the air will not be reduced until the saturation temperature is reached. As the temperature of the air is higher than that of the benzine, it may very well contain more gasoline vapours than indicated by the vapour-pressure curve, thus making $k>1$.

k was calculated on basis of a graphical determination of the item $p_1 \cdot (1 + t_n/273)$ as well as of the item π_n.

The example below will show the calculation of k for the test series compiled in Table XVII. The curves are shown in Figs. 15 and 16.

Calculation of K (*Table XVII*).

p_n (water)	50	235	435	645	830	920
p_n (Hg) + 760	756·7	777·9	793·1	809·0	823·1	829·9
t_0 (surface)	18·4	19·75	20·75	22·05	23·35	23·8
t_n (air)	18·4	21·7	24·45	25·55	26·25	26·6
t_n corrected (+0·8°) . . .	18·4	22·5	25·25	26·35	27·05	27·4
(π_n (mm Hg)	255	268	278	290·5	303·5	308
$p_1 \cdot 273 + t_n/273$ . . .	—	768·5	776·5	780	782	783
$p_n - p_1 \cdot (1 + t_n/272)$ . .	—	9·4	16·6	29·0	41·1	46·6
$(\pi_n - \pi_1) = \delta_n \pi$ . . .	—	13	23	35	48·5	53
$k = (p_n - p_1)(1 + t_n/(272)\delta_n \pi$.	—	0·72	0·72	0·77	0·85	0·88

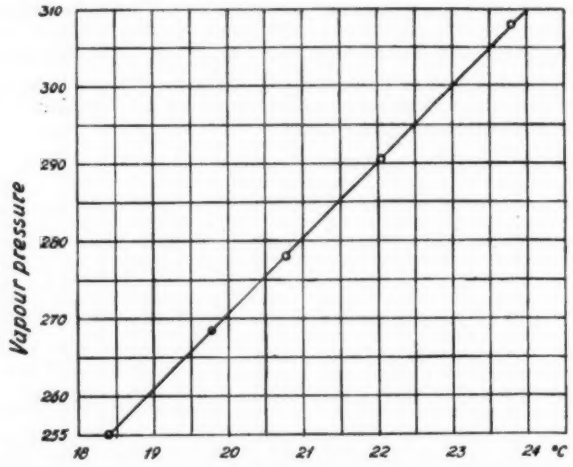

FIG. 15.

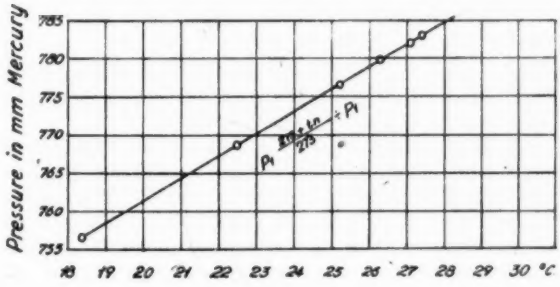

FIG. 16.

PRACTICAL EXPERIMENTS.

In order to carry out practical experiments a 2200-m^3 tank at an installation was used. Values corresponding to the laboratory experiments are impossible in large tanks, and the temperature was therefore measured by four resistance thermometers coupled to a registering galvanometer. The thermometers were of the iron wire type of 100 Ω and waterproof, the galvanometer being a cross coil instrument.

One thermometer was attached to a float, so that the horizontal resistance element was located in the gasoline surface, and two were suspended in the air space, one at the top of the tank and the other half-way between the benzine surface and the top. The fourth thermometer was placed outside the tank, at a shaded spot, for registration of the atmospheric temperature.

The thermometers in the tank were connected by insulated wires with the terminal box in the tank roof, from which cables led to the galvanometer. In order to prevent the wires of the floating thermometer from submerging in the gasoline when new quantities were pumped in, the float was counterpoised as shown in Fig. 17.

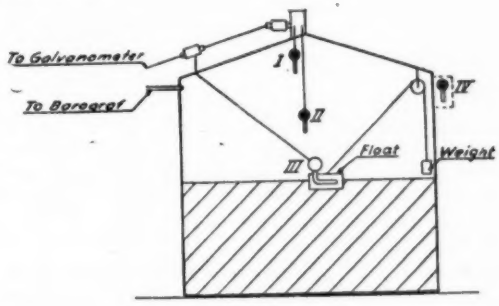

FIG. 17.

Pressure variations were recorded by a barograph consisting of an iron U-pipe containing mercury, and indicating the difference between the pressure in the tank and that of the surrounding atmosphere.

The placing of the thermometers was planned according to the following considerations :

(*a*) Heating is mostly due to the sun, and the thermometers were placed on the centre line so that their reaction would be independent of whichever side of the tank was the warmest for the time being;

(*b*) Rather large quantities of heated gasoline are conveyed to the surface, and consequently there is no reason to presume that the surface temperature will show any particular variation at different points. The tank side facing the sun will be heated both over and below the surface, and the heated gasoline will rise along the tank side and spread all over the surface.

(*c*) The thermometers recording the air temperature were placed one directly below the roof, and the other just below the midway point between the roof and the surface. The upper thermometer does not record the highest temperature of the air immediately under the roof plates, but it should show the mean temperature of the warmest part of the air, while the lower thermometer should show the mean temperature of the colder part of the air.

In order to correct or verify the mean temperatures measured, blank tests were made with water by pumping the gasoline into another tank on completion of the experiments. The tank was then cleansed and gas-freed and the gasoline quantity substituted by water. The temperature-pressure variations are shown in Tables XIX and XX.

TABLE XIX.

p mm petroleum.	0.	65.	85.	100.
t_1 upper tank air	15·2	17·3	17·5	17·8
t_2 middle tank air	15·0	16·2	16·3	16·6
t_3 surface	13·3	15·5	15·5	15·6
t average	15·10	16·65	16·90	17·20
t calculated	—	16·60	16·90	17·20

TABLE XX.

p mm petroleum.	70.	190.	250.	260.
t_1	6·2	11·6	13·1	13·2
t_2	6·2	11·5	12·9	13·0
t_3	9·0	11·0	12·5	12·6
t average	6·2	11·55	13·0	13·1
t calculated	—	11·75	13·05	13·2

When plotted, these values fall closely on the curve of the theoretical pressure increase, and this agreement between found and calculated values raises the question as to whether such a degree of exactness in the measurements can be possible. The scale of the registering thermometer is divided into intervals of 2 degrees, and the probable reading error therefore cannot be less than 0·2° C. The variations shown by the measurings are all within this limit.

The measurings were made at increasing temperatures. At falling temperatures, and especially during frequent, quick changes due to sunshine with drifting cloud, a corresponding agreement will not be obtained. Variations between the measured and the calculated temperatures of up to 2° C may be encountered.

Fig. 18 shows a pressure and temperature diagram of the tank when containing water. It will be noted that the temperature varied considerably during the day; the weather alternated between cloud and brilliant sunshine.

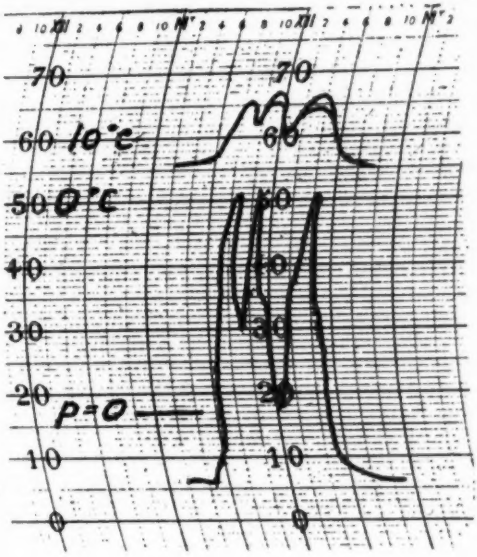

FIG. 18.

The curves on Fig. 19 constructed on the basis of Fig. 20 clearly show that at rising temperatures the temperature and the pressure will follow the theoretical curve very closely, while at decreasing temperatures the fall in pressure is larger than that corresponding to the temperature fall.

This is not really surprising, as it cannot be expected that the cooling of the tank air will take place in the same way as the heating. However, this has no influence on the results of the experiments, as all measurements were made at rising temperatures.

If the laboratory experiments with water (Fig. 14) are examined, it will be seen that the thermometer recordings are correct, provided that the starting point is chosen some time after the heating has been commenced.

This may perhaps explain why found and calculated measurements in tanks containing water show such a close agreement. The tank experiments were always commenced some time after sunrise—*i.e.*, well above the

beginning of the curve. The experiments show that the mean temperature registered by the thermometers at increasing temperatures is exact, and that consequently the placing of the thermometers was correct.

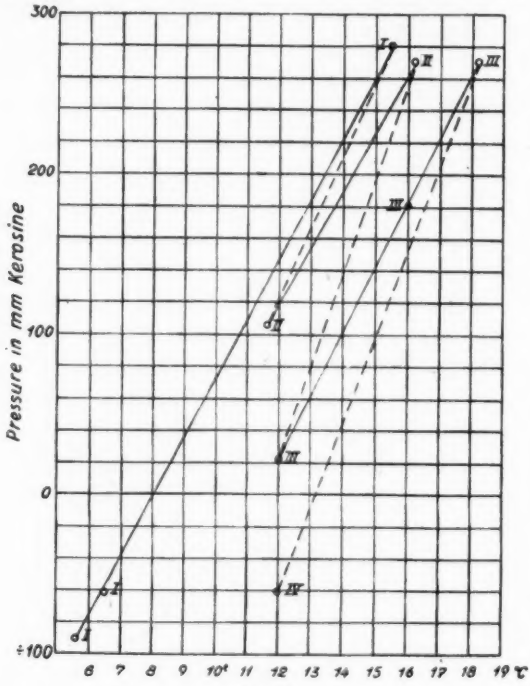

FIG. 19.

As the tank pressure valve will lift at approximately 300 mm, the measuring is limited to the temperature interval corresponding to this pressure.

In order to obtain the greatest possible accuracy in the experiments, the corresponding pressures and temperatures are read simultaneously under suitable circumstances.

A morning with sunshine offers the best conditions, as the tank has reached a temperature equilibrium overnight. Table XXI shows values measured on such a morning.

TABLE XXI.

Time.	8.00.	8.45.	9.00.
Pressure, mm Hg	7·6	21·0	21·3
Temperature tank air, top . . .	2·4	7·5	7·8
„ „ middle . . .	2·4	6·6	6·8
„ surface	4·6	6·2	6·2
„ atmospheric air . . .	2·5	2·6	2·6
Correction factor k calculated . . .	—	0·57	0·52

These values agree very closely with those measured by the laboratory apparatus. The heating of the tank was rather slow, as well over two hours passed from the time when the pressure in the tank was 0 until the tank valve lifted.

Another test showed the following results :

TABLE XXII.

Time.	8.15.	8.45.
Pressure, mm Hg	0	20·1
Temperature tank air, top . . .	2·5	8·1
,, ,, middle . . .	2·5	9·1
,, surface	4·4	6·4
,, atmospheric air . . .	2·4	2·4
k calculated	—	0·28

The tank air was heated quickly, and the correction factor was low. This may be due to three different causes. If the thermometers in the air do not register the mean temperature of the tank air, k will be too low or too high according to whether the mean temperature is lower or higher than that registered by the thermometers. If the recordings of the thermometers are correct, the low k value may be due to the fact that the higher gasoline concentration corresponding to the increase in the surface temperature has not had time to spread itself owing to the quick heating.

A slow heating, when the sun was dimmed by light clouds and therefore had little power, showed the following results :

TABLE XXIII.

Time.	7.00.	10.30.
Pressure, mm Hg	−6·1	+10·9
Temperature tank air, top . . .	2·5	6·0
,, ,, middle . . .	2·5	6·6
,, surface	4·4	6·0
,, atmospheric air . . .	2·0	2·0
k calculated	—	0·50

The tank air was often analysed the morning after a cold night, when there was no sunshine, so that the temperature would be the same as during the night. Two series of analyses showed the same results :

TABLE XXIV.

Temperature tank air, top . . .	2·5	2·5
,, ,, middle . . .	2·5	2·5
,, surface	4·4	4·4
,, atmospheric air . . .	2·4	2·3
Orsat tank air, at top	24·6	24·5
,, ,, at bottom . . .	26·4	26·4

The results of the analyses agree very closely with the gasoline vapour pressure corresponding to the temperatures prevailing.

As soon as the sun is shining, the equality is disturbed as shown by Table XXV.

TABLE XXV.

Time.	7.00.	10.15.	1.30.	Temp. of sample.
Pressure, mm Hg	−6·1	20·1	—	—
Temperature tank air, top	2·3	12·6	27·0	—
„ „ middle	2·4	12·0	21·5	—
„ surface	5·2	7·5	10·8	—
„ atmospheric air	2·4	4·0	8·0	—
k calculated	—	0·33	—	—
Orsat per cent at top of roof	—	25·1	25·4	30·5
„ „ „ „ tank side	—	25·0	25·0	20·0
„ „ „ bottom	—	25·0	25·8	4·1

The Orsat percentage at the top of the roof is measured in the pressure valve. It will be noted that the concentration in the tank air is nearly uniform, and that the change in concentration is small even at a temperature increase of 25°.

Simultaneously with the sampling, the temperatures at the sampling points were measured.

The pressure and k are not indicated for the last column, as the tank had " blown."

It will be seen that the Orsat percentage measured approximately 15 cm from the gasoline surface does not at all correspond to the vapour pressure of the gasoline at the gasoline temperature—it ought to be approximately 31 per cent—while it corresponds to the saturation percentage at the air temperature 4·1°, which according to the vapour-pressure curve is 25·8. Quite similar results were shown by the series of experiments mentioned in Table XXVI.

TABLE XXVI.

	Temperature.	Orsat percentage.
Tank air, top	6·0	—
„ middle	6·0	—
Surface	6·5	—
Atmospheric air	2·0	—
Pressure valve	6·0	24·8
Sampling point, top	5·7	25·1
„ „ bottom	3·6	25·5

The bottom Orsat analysis—15 cm above the gasoline surface—corresponds to the saturation at the measured temperature, 3·6°, which is 25·3 per cent.

It therefore seems that the explanation must be that : when the tank air is heated, which is always from the outside and usually unilateral, a layer of cold air quickly covers the gasoline surface and to a great extent prevents

the evaporation which otherwise would have taken place due to the higher vapour pressure caused by the heating of its surface. The experiments show that in the formula for the " breathing loss " a correction factor must be applied in the vapour-pressure item. Under normal conditions this correction factor will have a value of about 0·5.

Determination of Small Losses.

The described method of determining the saturation percentage may be used for measuring very small evaporation losses.

If a series of saturation percentage determinations are made with one sample of gasoline, and the ratio of the air/gasoline-vapour volume to the gasoline volume is known in each case, the quantity evaporated at each determination may be calculated and the curve saturation percentage versus evaporated quantity may be drawn.

If this curve has been found for the gasoline in the main tank of the installation, it is also possible, by measuring the saturation percentage of a sample passing through the installation, to determine from the curve the evaporation up to the point of sampling, provided that the saturation percentage is determined at the same temperature and at the same ratio of gasoline/air mixture to which the curve applies.

During the experiment the sample used for determining the saturation percentage has lost a percentage corresponding to the air volume, and it would be reasonable to extrapolate to the saturation percentage recorded for a benzine sample large enough to show the evaporation loss 0. This, however, is not necessary, provided that the gasoline/air volume ratio is the same at each determination of the saturation percentage.

A series of tests have been made with gasoline from a large installation. The samples were taken in cans rinsed with the gasoline being sampled and shaken so that the air content was gasoline saturated. The cans were then filled from the bottom by syphon.

Samples were taken from a main tank, from a recently filled road wagon, one compartment filled by undersurface loading, one by splash loading, and from a newly drawn can. The results of the analyses are shown in Table XXVII.

Table XXVII.

Saturation Percentage.

Sample.	Gasoline, ml.	Air mix, ml.	Orsat, per cent.	Temp., ° C.	On Fig. 20 marked.
Main tank	250	130	36·1	—	—
Tank wagon (undersurface loading)	250	105	35·8	—	a
Tank wagon (splash loading) .	250	135	34·8	16·1	b
Can	250	115	35·6	—	c

Table XXVIII shows the determination of the curve of saturation percentage/evaporated quantity :

TABLE XXVIII.

No.	Gasoline, ml.	Air mixture, ml.	Orsat, per cent.	Evaporated, per cent.	Temp. ° C.
1	250	130	36·1	0·82	—
2	250	135	34·6	0·80	—
3	250	130	33·6	0·75	16·1
4	250	140	32·8	—	—

The corresponding curve is plotted on Fig. 20. If the values from Table XXVII (*a*, *b*, and *c*) are inserted it will be observed that in the case

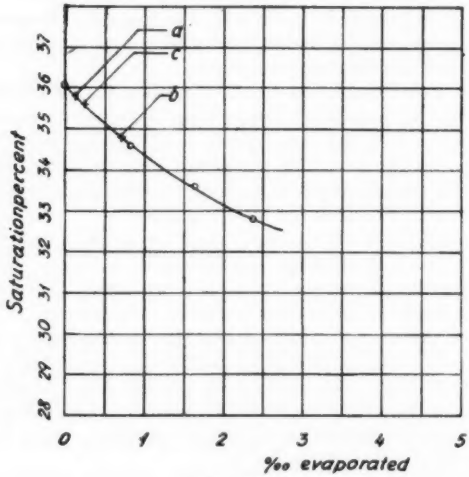

FIG. 20.

of the splash loading of the tank lorry (*b*) 0·7 per cent is lost, against only 0·15 per cent in the case of the undersurface loading (*a*), values which correspond very closely to the losses measured by rail tank-car loading, Table IX. When filling a can (*c*) 0·22 per cent is lost—*i.e.*, approximately 1·5 times as much as when undersurface loading a tank lorry.

This is in accord with the fact that the cans are filled through a measuring apparatus, which will cause a small extra loss, and that undersurface loading is not so efficient when applied to cans as when applied to tank lorries.

The results obtained show that the method is reliable but it was considered that it involved too many operations—*i.e.*, sample drawing, the making of a saturated air mixture, and finally the analysing of this by the Orsat apparatus.

Furthermore, there is no indication of the air mixture being completely saturated, and this reduces the reliability of the results considerably.

The Orsat analyses would be unnecessary if the increase in volume of the air sample could be measured during the saturation. The apparatus in

Fig. 21 was therefore constructed. A 100-ml Orsat measuring cylinder (1) with the 50-ml mark on the narrow part is connected through the cocks (6) and (7) with the container (2), in which the air/gasoline-mixture is made, and which is filled with thin glass tubes giving a large surface for speeding up the saturation.

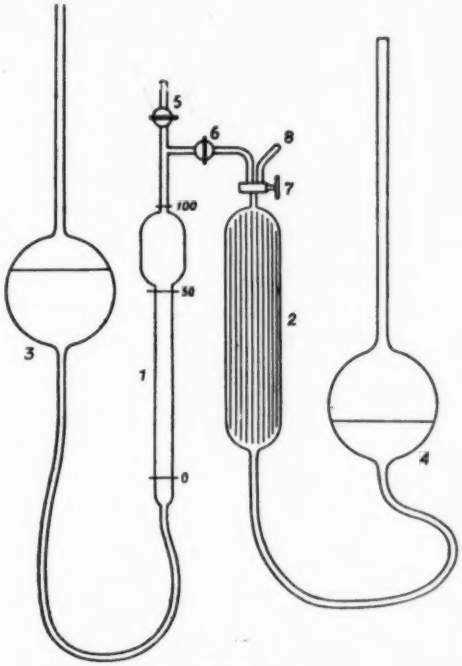

FIG. 21.

On the container the contents are marked from the top, 50 ml, 75 ml, and 100 ml, but these measures do not need to be very accurate. The measuring cylinder and the container are connected with two level flasks (3) and (4), and the sealing liquid is a strong solution of sodium chloride.

Cock (5) is for drawing in the air sample and for expelling the air mixture when the test is finished. Cock (7) is a three-way cock connecting the container with either the measuring cylinder or the pipe (8) through which the gasoline sample is drawn in. All the connecting pipes are of 1·5-mm bore, and all connections are made with benzine-resistant synthetic rubber.

The whole apparatus must be placed in a constant-temperature water-bath as shown in Fig. 22.

The cock (7) is turned to make connection between the container (2) and the pipe (8), and both are filled with sealing liquid. Through (8) a sample of the gasoline is drawn in to the mark required. It is important that no air is drawn in and any air bubbles must be expelled through (8).

The cock (7) is then turned connecting (1) and (2), the cocks (5) and (6) being shut. In the measuring cylinder (1) the air volume required is drawn in and the volume (b_1 ml) ascertained; the air is then forced through the cock (6) into (2) for saturation with gasoline vapour. It is necessary to draw the air sample back in the measuring cylinder and again press it over into (2) several times in order to reach complete saturation, and this procedure must be continued until two readings of the final volume are identical.

The measuring cylinder is graduated from the lower end, the reading (a) therefore giving the number of ml by which the air-mixture is less than 100. As we start with b ml air, the volume increase will be $((100 - a) - b)$ ml and the percentage of gasoline vapour in the mixture will be

$$(100 - b - a)100/(100 - a) \text{ per cent}$$

The vapour pressure of the gasoline expressed in atmospheres at the temperature in question will be

$$[(100 - b - a)/(100 - a)] \,.\, [\text{bar press}/760]$$

Tests have been made with this apparatus in order to ascertain whether the analysis could be made within a reasonable time and sufficient accuracy, the results for five different samples being given in Table XXIX.

TABLE XXIX.

Sample.	Air volume b, ml.	Temp., ° C.	Reading a, ml.	$100 - a - b$, ml.	Saturation, per cent.	Orsat, per cent.
A_1	50	19	20·2	29·8	37·4	37·5
A_1	50	19	20·2	29·8	37·4	37·4
A_2	50	19	19·8	30·2	37·7	37·8
A_3	50	17·5	25·4	24·6	32·95	33·0
B_1	50	20·0	27·9	22·1	30·6	30·6
C_1	50	15	27·5	22·5	31·1	31·1

The conformity between the saturation percentage formed and the Orsat analysis is satisfying, and shows that the method gives sufficiently accurate results. An analysis can, if temperature is not to be controlled, be executed in about 15 minutes.

The sources of errors are few, but there is one that is rather deceptive. The first analyses made showed good conformity with the Orsat analyses, but thereafter a whole series of tests showed a lower saturation percentage than the corresponding Orsat percentage. The first idea was that leakage might be the cause, but the apparatus proved to be absolutely tight; accordingly the error must have some other origin.

The saturation percentage cannot be too small unless in the equation above the denominator is too big and/or the numerator too small.

The denominator can only be too big by misreading, which can be avoided, and the error must therefore be placed in the numerator $(100 - a - b)$, or rather in the volume b. Misreadings were out of the question, and the volume could only be altered either by leakage or by some of the air being dissolved in the gasoline. It was not possible to find any record supporting

this theory and furthermore the first and the correct analyses disproved the idea.

It was found that the error was caused by a drop of gasoline seeping into the measuring cylinder and spreading over the glass surface. When measuring out the air volume a little of the gasoline evaporated, and accordingly the air volume b was reduced by the volume of that gasoline vapour, whereby the measured increase in volume was found to be too small. After a rinsing of the measuring cylinder with sulphuric and chromic acid the apparatus again proved correct.

It is a source of error which is difficult to identify without the use of the Orsat analysis.

In order to avoid this it is advisable to " flush " the measuring cylinder before the analyses with air, and by its smell satisfy oneself that the air contains no gasoline vapour.

If the walls of the measuring cylinder are not uniformly wetted by the sealing liquid, this indicates that the cylinder should be rinsed with sulphuric and chromic acid.

In order to determine the curve that shows the relation between the saturation percentage and the amount of gasoline evaporated, several analyses are carried out with the same sample in the container, but each time with new air. The calculation of the amount of gasoline evaporated at each determination is as follows :

Let c be the number of ml gasoline in the container.
Let b be the amount of air for each analysis.
Let a be the final reading in each analysis.

The molar weights of the first evaporated fractions are about 70, and the specific gravity very near 0·7. 1 ml of gasoline will then weigh 700 mg, and in vaporized state at 0° C and 760 mm pressure have a volume of $(700/70)22{\cdot}4 = 224$ ml.

The measured increase in volume $(100 - a - b)$ is gasoline vapour and would at 0° C fill $(100 - a - b)273/(273 + t)$. The pressure correction is so as to be negligible.

In the liquefied state the gasoline volume will be

$$(100 - a - b)273/(273 + t)224 \text{ ml}$$

and the vaporized amount will be

$$(100 - a - b)273 \,.\, 1000/(273 + t) \,.\, 224 \,.\, c \text{ per cent}$$

For the gasoline in question it is possible from the calculations to construct the curve which gives the relation between the amount evaporated in per cent as abscissa and the saturation percentage as ordinate. If five or six values are determined it is possible to extrapolate for the volume per cent evaporated—*i.e.*, the saturation percentage that would be found if the amount of gasoline was unlimited.

It must be remembered that the curves are usable only at the temperature at which they are determined, and that a temperature increase of 1° C can give a variation of 1 or 2 units in the saturation percentage. As the vapour-pressure variation with the temperature is not known, it is not possible to make a temperature correction, and it is therefore essential

that the temperature be kept constant. The variation should not exceed 0·1° C.

It is easiest to work in a thermostat as near as possible to room temperature, and it is very important that both air and gasoline be at the same temperature.

Table XXX gives the results of a test series with a gasoline sample taken directly from an ocean installation.

TABLE XXX.

Temperature t = 20° C. Air volume b = 50 ml. Gasoline volume c = 75 ml.

Analysis No.	Reading a, ml.	Increase of volume.	Saturation, per cent.	Evaporated partial, per cent.	Evaporated total, per cent.
1	26·9	23·1	31·6	1·38	1·38
2	27·7	22·3	30·8	1·24	2·62
3	28·2	21·8	30·4	1·21	3·83
4	28·5	21·5	30·05	1·20	5·03
5	28·6	21·4	29·8	1·18	6·21

As a check an Orsat analysis was made with the mixture from test No. 5, and showed 29·8 per cent in full agreement.

Table XXXI gives results for the same gasoline, but after it had been stored for a fortnight in a half-filled closed can.

TABLE XXXI.

Temperature t = 20° C. Air volume b = 50 ml. Gasoline volume c = 75 ml.

Analysis No.	Reading a, ml.	Increase of volume.	Saturation, per cent.	Evaporated partial, per cent.	Evaporated total, per cent.
1	27·9	22·1	30·6	1·22	1·22
2	28·5	21·5	30·1	1·18	2·40
3	28·8	21·2	29·8	1·17	3·51
4	28·9	21·1	29·7	1·17	4·75

As a check Orsat analyses were made with the air mixture from test No. 1 and 4, and showed 30·6 and 29·75 per cent.

If the saturation percentage from the two tables are plotted against the corresponding percentage total evaporated, and the saturation percentage for the evaporation percentage is extrapolated, the curves in Fig. 23 will appear. If the abscissae in curve II are increased by 2·1 per cent the values will coincide with curve I, as shown by the points marked 0. This means that the sample has lost 2·1 per cent by standing in a closed can for a fortnight, and it emphasizes the importance of care in taking and keeping samples. For evaporation investigations at a tank installation the curve for a gasoline sample from the main tank is determined, and it is thereafter possible by a saturation percentage determination of a sample from any point of the installation to read from the curve how many parts per million the gasoline has lost up to this point.

Care must be taken in the drawing of samples, the best way being to fill the sample container with water which is run out as the sample is going in, thus avoiding any evaporation. Alternatively the container should be rinsed several times with a little gasoline, and then filled completely with

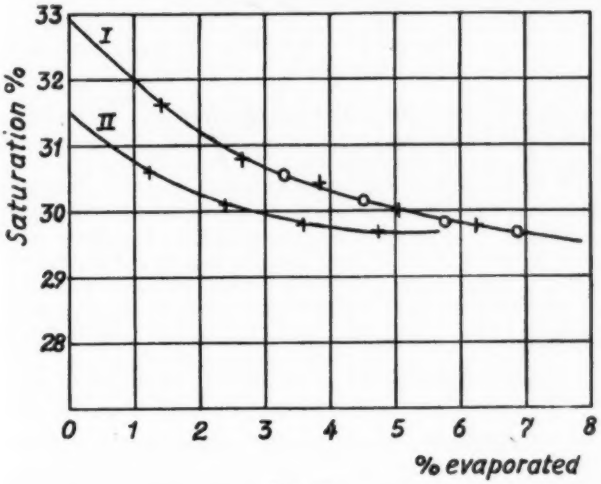

FIG. 23.

the sample through a pipe carried right to the bottom. No airspace should be left above the sample.

Temperature variation during the tests should not exceed 0·1° C.

Care must be taken that the samples taken are identical apart from any evaporation which has taken place.

DETERMINATION OF THE MEAN TEMPERATURE.

The determination of the quantity of gasoline in a tank is difficult. A method suggested by Mr. Syndergaard provides a continuous gauge glass from the bottom to the top of the tank so that the height and the temperature of a gasoline column can be measured while it is in equilibrium with the gasoline level of the tank.

The applicability of the method relies on the contents of the tank being homogeneous, so that there will be no difference, except in the temperature, between the tank content at various heights.

If a liquid column with the height h_1 has been measured at t_1° C, and it is desired to ascertain the level h_2 at t_2° C, this will be

$$h_2 = h_1 \cdot (1 + 0{\cdot}0011(t_2 - t_1)),$$

as the expansion coefficient of benzine is 0·0011.

This formula and Syndergaard's sounding method, however, solve another problem, which may cause great difficulties—*i.e.*, the determination of the mean temperature of a tank.

It is not possible to make a gauge glass in one piece from the top to the bottom of a large tank, so ordinary gauge glasses are connected together with copper tubes, as shown in Fig. 24. If the bottom and top cocks alone are open to the tank, and the cocks between the glasses are open, the gauge-glass system will work as one continuous glass.

as

$$h_2 = h_1(1 + 0{\cdot}0011(t_2 - t_1)),$$
$$t_2 = t_1 + (h_2/h_1 - 1)/0{\cdot}0011,$$

h_1 and t_1 are measured in the continuous gauge glass. If therefore h_2—the liquid level in the tank—can be measured, the mean temperature t_2 may be calculated. h_2 can be measured when the gauge glasses are made to be used either as a continuous glass or as normal glasses. If only the top-most glass, which is still connected with the liquid, is used, that is if the cock from the glass to the tank is open, and the cock to the glass below is closed, and if care is taken to keep close to the same temperature in the glass as in the upper part of the tank content by emptying and refilling the glass several times from the tank, the level in the glass will be the height sought—" h_2 "—and the mean temperature may be calculated. This is of great importance in practice, as every exact determination of the volumetric tank content involves a temperature determination.

Combating the Breathing Loss in Practice.

As mentioned in the introduction, the evaporation and breathing losses are the most important factors of the whole leakage problem. Many methods of reducing these losses have been suggested, and several have been put into practice.

If a gasoline depot with all its appurtenances is regarded as one unit through which a certain quantity of gasoline is passing, it will be seen that a considerable part of the evaporation loss occurs when the gasoline is being transferred from one place to another. When gasoline is transferred from one container to another, fresh air will be drawn into the first container and gasoline/air mixture will be expelled from the other. The idea naturally suggests itself that the two containers should be connected with a pipe so that the benzine/air mixture would merely change its place.

Theoretically it should be possible to avoid gas loss entirely by placing gas pipes everywhere, but this cannot be carried out in practice.

As mentioned, the breathing loss has a very great influence on the leakage, but will not be affected by gas pipes placed as suggested. Under normal conditions a certain quantity of gas must escape from a tank installation and it is important to reduce this as much as possible and to ensure that it has the smallest possible gasoline content. The investigations show that the gas escaping from the tank car, when the filling is properly directed, is far from saturated, while several analyses have shown that the air in the tanks contains far more gasoline vapour. It would therefore be advisable to let the air contained in the barrels, drums, and tank cars escape, and to preserve the tank air.

As a result of these deliberations a large gasoline installation was fitted with a gas-pipe system in March 1938.

The installation, which is supplied by sea, consists of two 2200 cu m, and one 1100 cu m main tanks, as well as four 22-cu m filling tanks.

The tank roofs and all the fittings are gas tight, and the tanks are provided with gauge glass, making it unnecessary to open them for sounding.

The gas pipe to the main and filling tanks was made of 3-inch pipes, each main tank being provided with a valve by means of which it may be cut off from the gas system.

The tanks are provided with glycerine vacuum pressure valves, which will open at 250 mm over pressure and 50 mm under pressure, both in mm water column. The idea of the system is that the gasoline supplied by the installation will compensate for part of the breathing loss. In the morning the tanks will either have an under-pressure or a very low over-pressure in accordance with the low night temperature. The pumping of gasoline from the main tanks to the filling tanks will not change the pressure, and no gas will escape. At the same time as the day temperature exerts its influence, gasoline will be discharged from the filling tank, and the resulting increase in the air volume will take up part of, or all, the tank-air expansion caused by the rise in temperature.

At the installation in question the introduction of the gas pipe system showed a very favourable result, as the breathing loss almost completely disappeared. The total loss, which in former years had been very constant, and rather *low*, was during the course of the year reduced by 50 per cent, while two other installations, which were not provided with gas pipes, showed the same leakage as in the preceding years. The reduction must therefore be due to the gas pipes, and not to fortuitous weather conditions.

An idea of the importance of the gas-pipe system may be formed by comparing the temperature–pressure variations in a tank when cut off from, and when inserted in, the gas system.

Even if the same variations will not be obtained on two different days, it will be seen that the temperature variations, which will make the over-pressure valve lift when the tank is cut off from the gas system, will be compensated for by the discharged quantity, when the tank is connected in the gas system, in which case the maximum pressure will not be reached.

Fig. 25 shows the pressure diagram for 1½ weeks with the gas installation working. The corresponding temperature curves are plotted on the pressure diagram, as the original temperature curves cover 48 cm per 24 hours, and accordingly cannot be reproduced. The dotted temperature curve shows the surface temperature of the gasoline, while the full lines show the curves of the two thermometers in the tank air. The ordinate is 1 mm per degree C.

In the pressure diagram the zero line (atmospheric pressure) is off the 10-line, and approximately 15 mm corresponds to 100-mm water column.

The following points on the diagrams may be observed. The first two days the tank is cut off from the gas system, and the pressure valve will " blow " at a rise in temperature of the warmest thermometer of approximately 12° C. The first day (Thursday) the tank has " blown " for approximately 1 hour, after which the temperature falls. The second day the tank " blows " for 4 hours, and owing to the low night temperature it draws in air during the course of the night. The pressure curve falls to the

minimum pressure of the vacuum valve, and is flat for a long period. The third day the tank begins to "blow," but at point (*a*) it is connected through the gas pipes with the other tanks from which gasoline is discharged.

The pressure drops immediately, and will continue falling during the rest of the day, in spite of the fact that the temperature of the tank air is still increasing for approximately 2 hours after the gas connection has been established.

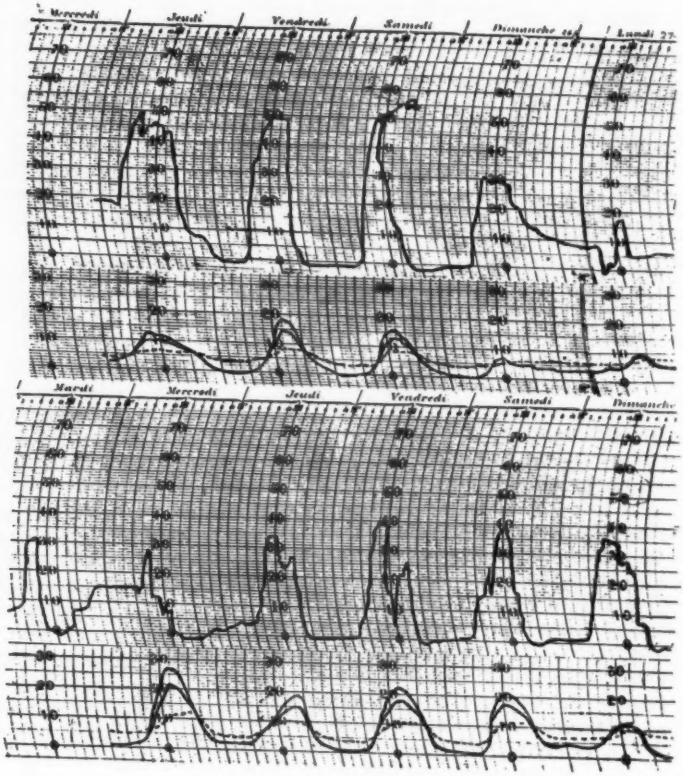

FIG. 25.

On Sunday and Monday the weather was cloudy, and the increase in pressure was therefore small. On Tuesday the temperature registration did not work, but nothing of importance happened, the weather being similar to that of the preceding Saturday.

On Wednesday the weather was fine, with sunshine all day and only little wind, the tank air temperature reached 27° C, but great quantities of gasoline were discharged, including a rail tank car (15,000 litres), and the pressure was kept down.

Friday was characterized by a heavy fall in pressure a little before noon.

Rail tank cars and tank lorries were filled at that time, the temperature of the tank air was still increasing, and during the lunch time the pressure rose again. It will be seen that had there been no discharge of gasoline with the corresponding fall in pressure, the tank would have " blown " shortly before noon. The temperature and the pressure correspond very well with the conditions observed on the preceding Friday, when no gasoline was discharged, and the tank " blew " for 4 hours.

The gas-pipe system is no universal remedy against leakage, and it must be adapted to the conditions prevailing at each individual installation. It will be seen, however, that whenever the conditions are favourable, the system will give excellent results.

Before deciding where to place the gas pipes it is necessary to find out by Orsat analyses where the losses occur, and their magnitude. With the principle in mind that the unavoidable air loss must be concentrated at the places where the vapour contents of the gasoline/air mixture are smallest, it will not be difficult to place the gas pipes in the right position, so that the losses will be as small as possible.

It is a presumption, of course, that the measurings will show that the individual operations are carried out in such a way that no unnecessarily high vapour concentrations will arise.

Moreover it is necessary to make a survey of costs and savings as the gas pipes involve expenditure, and they must result in a net saving.

The situation may perhaps, be further explained by an examination of the example mentioned. The tank capacity is, as mentioned, 5,500 cu m, and the quantity of gasoline passing through the installation every year is well over 20,000 cu m. Under normal conditions the total loss was around 160,000 litres—*i.e.*, 0·8 per cent. By means of gas pipes the loss was reduced by 70,000 litres, and this economy was obtained by a capital expenditure of 4000 to 5000 Kroner in all. The working expenses of the system are negligible.

What will be the expenses of a further reduction of the loss, and to what point can the loss be reduced? The remaining loss, approximately 90,000 litres, consists of gauging loss, temperature loss, and a small evaporation loss. The gauging loss cannot be less than 0·2 per cent, as the legal margin for gauges in Denmark is 0·5 per cent, and the temperature loss—*i.e.*, the loss derived from delivering the gasoline at a lower mean temperature than that at which it was imported—varies somewhat from year to year, but may be estimated at 0·1 per cent. In all, 0·3 per cent, or 60,000 litres, are unavoidable. The quantity left is 30,000 litres, which at a sale price of 25 Øre per litre represents a value of 7500 Kroner. It will easily be seen that the saving obtained from the installation and operation of complicated apparatus will not be large enough to make it remunerative.

At an import station, for instance, it will hardly pay to place gas pipes from the main tanks to the vessel. Such pipes would need to be of 6 to 10-inch diameter, owing to the pumping capacity of the vessel (100–300 tons per hour), which makes them expensive. It is scarcely possible to form a reliable picture of the evaporation due to the discharge of a tank vessel, as the holds are so large that a reasonable number of analyses will offer no correct basis for the judgment, but a number of investigations made when discharging rail tank cars and tank lorries show that the vapours

developed are far from saturated. Consequently there is no reason to presume that the air in the tank vessel is saturated, a fact which will greatly influence the saving that might be obtained from gas pipes. On the whole, it is important to examine very carefully the possible saving before venturing on heavy installation expenses.

The loss arising from the pumping of benzine out of a tanker is very conspicuous, because it is a rather considerable quantity, which disappears at once, but it is difficult to reduce the loss through reasonable expenditure. Thus it will not be an economic proposition to install gas pipes from the tanks to the vessel.

Of the factors which have an essential influence on the applicability of the gas system, there may be mentioned in the first place the volume of the quantity discharged as compared with the air volume. Large tank capacity with a small degree of filling and little discharge is the most unfortunate combination, and the gas pipes will be of little influence, as the small discharge can only compensate for a small part of the breathing loss, which will be considerable, owing to the large air volume.

Under such circumstances an endeavour can only be made to reduce the loss as much as possible by using one tank for each quality, and to keep the rest of the tanks either empty or fully filled. A filled tank will " breathe " very little, as the air space is small, and the empty tanks should be emptied completely and cut off from the gas system. Although an empty tank will " breathe," the " breathing " will cause no loss if the tank does not contain any benzine, while it will participate in the breathing loss with its whole capacity if it remains in the gas system.

An essential improvement of such unfortunate tank conditions might be obtained by combining with the gas-pipe system a tank insulated on the " Syndergaard " principle, *i.e.*, with reinforced concrete.

If there are several gasoline tanks at the installation, it will suffice to Syndergaard-insulate one of them—preferably the largest—and to operate with that tank exclusively. The other tanks are connected with this tank by gas pipes, and as far as possible are kept either filled—in the gas system—or completely empty and cut off from the system.

As there are practically no temperature variations in the Syndergaard-tank, the pressure increase caused by the rise in the temperature of the other tanks will be distributed on the extra air volume of the Syndergaard-tank, thereby compensating for a corresponding part of the loss.

After the installation referred to had been equipped with gas pipes, a number of analyses were carried out, most of which are without interest, although one of them deserves further comments.

The tanks had an under pressure of 40-mm water column (as the vacuum valves do not operate at less than 50 mm, no fresh air had been drawn in), and the Orsat percentage of the air was determined from the top of tank III. The analysis showed 19·0 per cent. By closing the gas-pipe connection with tank I and II, and by pumping gasoline from tank I to the filling tanks, the pressure in tank III was increased to + 120-mm water column, and the tank air was again analysed.

The Orsat percentage was now 22·4. The temperature was 7° C, and the saturation percentage of the gasoline in question was 20·2 at 7° C. The air from the filling tanks was supersaturated, because the pumping pipes

open out at the top of the tank; the same conditions that apply to the splash filling of rail tank cars.

As the tops of the main tanks do not normally contain fully saturated vapours, it is irrational to supply supersaturated air from the filling tank, but this was a detail which had been overlooked. As a result of this analysis—which was verified by several others—the pumping pipes of the filling tanks were altered. In consideration of the risk of fracture of the pipes, as for instance in the case of fire, the inlet at the top of the tank was retained, and the pipe was internally extended to the bottom. By a ½-inch perforation of the pipe directly below its inlet the syphon effect was counteracted.

Gas pipes are not at all a new invention. They have been proposed and used numerous times, but as far as is known no system has formerly been used, by which the benzine discharged has been exploited for a total or partial compensation of the breathing loss.

It is difficult to free oneself from the idea that whenever the effect of the gas pipes has not been quite satisfactory the problem of placing them has not been thoroughly investigated and considered prior to their installation. *National Petroleum News* of June 10, 1936, contains an article: "New Methods of Reducing Vapour Losses in Truck Loading," in which four methods are indicated:

(1) filling through a permanently installed pipe to the bottom;
(2) filling through the bottom outlet valve;
(3) filling through the manhole with the filling pipe extended to the bottom;
(4) filling through the manhole with a rubber packed "helmet" over the manhole and return of the air to the main tank.

The saving obtained by these methods is estimated at 75 per cent.

(1) and (3) are identical, as it is immaterial, of course, whether the pipe to the bottom is permanently installed on the vehicle or not.

(2) is a method giving due consideration to the evaporation loss, while no attention is paid to the risk of losses involved by the procedure recommended. When filling the tank through the bottom valve it is possible that there will be a leak at the place where the filling hose is coupled to the discharge pipe, and moreover when the filling is completed, it will not be possible to empty the hose until it is disconnected from the tank.

If the hose has to be emptied, when disconnected, the loss may easily exceed the evaporation loss, which would result from splash filling.

(4) Does not serve the purpose, as clearly shown by the curves of the tank-car filling (Fig. 8). If the tank is filled from the top, a saturated or super-saturated air/gasoline-vapour mixture will be driven into the main tank, from which it will vanish through the breathing of the tank.

In the case of under-surface filling the air directed from the car back to the tank will serve quite the opposite purpose of what was desired, as the result is that a certain air/gasoline-vapour mixture with a small benzine content will be saved, while just as large a quantity of a higher gasoline concentration will be lost later.

It will thus be seen that there is every reason to consider all factors before installing gas pipes. In the writer's opinion they have only one justifica-

tion—and prospect of being useful—that is when they are used in the manner outlined above with due regard to the conditions prevailing at each individual installation.

A clearer survey of the matter may sometimes be obtained by making a diagram of the installation or a scheme similar to that previously outlined. The installation is measured thoroughly, and the results are plotted on the diagram, from which it will be seen immediately where the heavy losses originate and at which places efforts to reduce the loss should be contemplated.

Acknowledgment.

The author desires to acknowledge his indebtedness to Mr. Percy Ipsen, chairman of the United Oil Co., of Copenhagen, for his keen interest in the work, for the provision of opportunities and financial assistance necessary to complete it and for permission to publish the results.

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SOME OBSERVATIONS ON THE DEVELOPMENT OF EXTREME PRESSURE (E.P.) PROPERTIES BY CHLORINE AND SULPHUR ADDITIVES IN MINERAL OIL, AS ASSESSED BY THE FOUR BALL MACHINE.

W. Davey, B.Sc., Ph.D., F.R.I.C.

Summary.

The Four Ball Machine has been used to assess the development of E.P. properties by chlorine and sulphur additives in mineral oil and the use of these additives together for high load conditions justified. The formation of ferrous chloride films by chlorine additives has been confirmed and the effect of sulphide films and hydrogen chloride studied.

Introduction.

In two previous papers [1,2] the present author has used the Four-Ball Machine to assess the E.P. properties of some chlorinated compounds and to study the mechanism of reaction of reactive sulphur in mineral oil. Prutton, Turnbull, and Dlouhy [3] in a recent comprehensive paper have studied the mechanism of the development of E.P. properties by chlorine and sulphur additives separately and blended together in mineral oil, and have proposed mechanisms to account for the reactions which occur between these additives and iron. These authors demonstrated the formation of ferrous chloride by heating iron powder with the additive alone and with sulphur present, and showed that hydrogen chloride was liberated during the reaction. They suggest that hydrogen chloride is not a likely reaction intermediate, and conclude that when sulphur is present the formation of ferrous chloride is facilitated by the sulphide film formed. They further suggest that in view of the high temperatures produced under E.P. lubricating conditions the same reactions will occur, and in support of this suggestion were able to demonstrate the formation of chloride and sulphide on gear teeth during "shock tests."

In the present work the improved E.P. properties shown by combined chlorine and sulphur additives are demonstrated, and the results and conclusions of Prutton, Turnbull, and Dlouhy confirmed by the use of chloride and sulphide formed on the test balls. The part played by the liberated hydrogen chloride has also been studied, and the results obtained suggest that although it may play a part in the reaction to form ferrous chloride films at low loads, it is unlikely to be the intermediate responsible for film formation under high loads. Attempts to titrate the hydrogen chloride liberated from the decomposition of chlorine additives blended in oil were unsuccessful, but using neat chlorinated paraffin wax the amount of hydrogen chloride liberated was found to be approximately proportional to the applied load. This would indicate that breakdown of the additive is just sufficient to produce a film of the requisite thickness to carry the applied load.

Experimental.

In the work on the Four-Ball Machine the standard short duration test (60 sec.) was used throughout.

Section 1. *Comparison of the E.P. Properties of Chlorine and Sulphur Additives in Mineral Oil.*

Blends of free sulphur, benzyl disulphide, chlorinated paraffin wax, and benzo-trichloride in turbine-oil quality Duosol 65 oil were prepared and

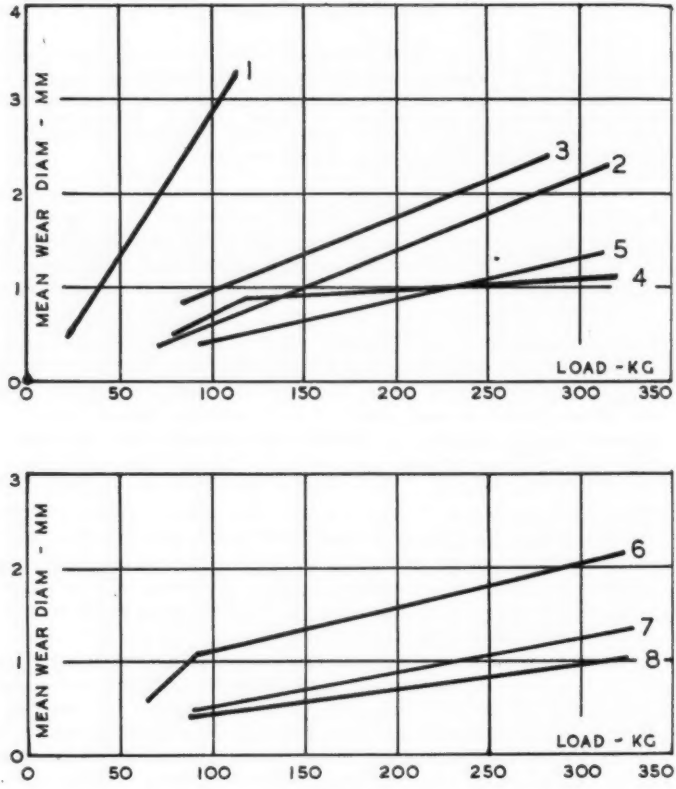


Fig. 1.

WEAR-LOAD DIAGRAMS.

1. Duosol 65.
2. ,, + 5% chlorinated paraffin wax.
3. ,, + 2% benzyl disulphide.
4. ,, +0·6% sulphur + 5% chlorinated paraffin wax.
5. ,, + 2% benzyl disulphide + 5% chlorinated paraffin wax.
6. ,, + 0·6% sulphur.
7. ,, + 5% benzo-trichloride
8. ,, + 0·6% sulphur + 5% benzo-trichloride.

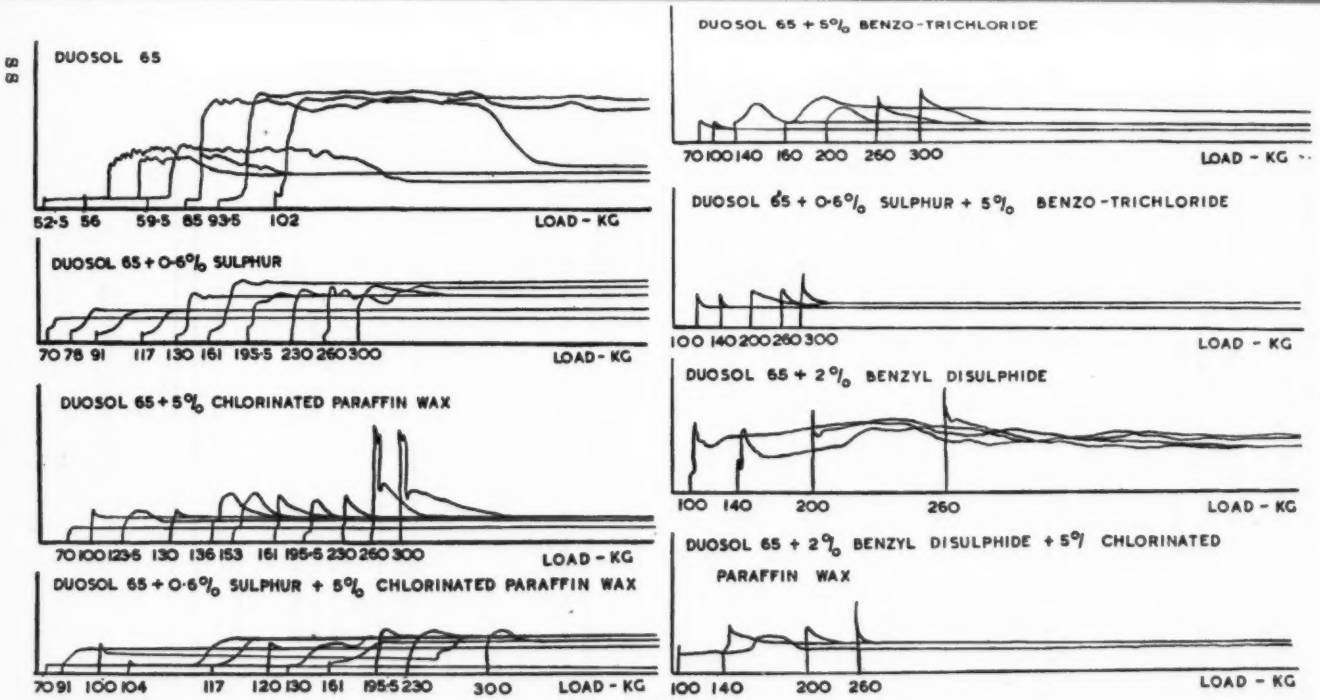

DUOSOL 65
52·5 56 59·5 85 93·5 102 LOAD - KG
DUOSOL 65 + 0·6% SULPHUR
70 78 91 117 130 161 195·5 230 260 300 LOAD - KG
DUOSOL 65 + 5% CHLORINATED PARAFFIN WAX
70 100 123·5 130 136 153 161 195·5 230 260 300 LOAD - KG
DUOSOL 65 + 0·6% SULPHUR + 5% CHLORINATED PARAFFIN WAX
70 91 100 104 117 120 130 161 195·5 230 300 LOAD - KG
DUOSOL 65 + 5% BENZO-TRICHLORIDE
70 100 140 160 200 260 300 LOAD - KG
DUOSOL 65 + 0·6% SULPHUR + 5% BENZO-TRICHLORIDE
100 140 200 260 300 LOAD - KG
DUOSOL 65 + 2% BENZYL DISULPHIDE
100 140 200 260 LOAD - KG
DUOSOL 65 + 2% BENZYL DISULPHIDE + 5% CHLORINATED PARAFFIN WAX
100 140 200 260 LOAD - KG

FIG. 2.

FRICTION-TIME CURVES.

Scale : 0·5 cm. vertical = 0·086 (coefficient of friction).

subjected to test. The results obtained are given in the form of wear/load diagrams (Fig. 1) and friction/time curves (Fig. 2).

Section 2. Effects of Ferrous Chloride and Sulphide Films.

Ferrous chloride films were prepared on oil-free test balls by heating them in a stream of pure, dry hydrogen chloride and sulphide films obtained on

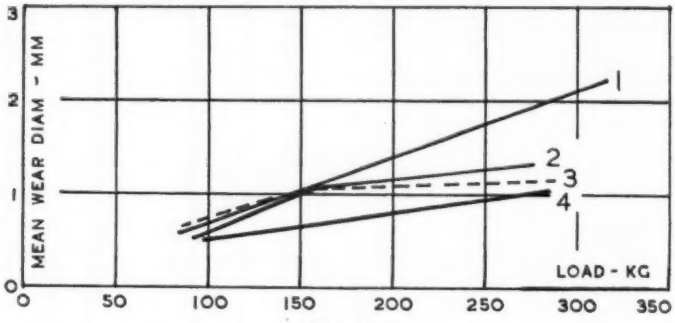


FIG. 3.

WEAR-LOAD DIAGRAM.

1. Untreated balls—Duosol 65 + 5% chlorinated paraffin wax.
2. Ferrous chloride film—Duosol 65.
3. Ferrous chloride and sulphide film—Duosol 65.
4. Ferrous sulphide film—Duosol 65 + 5% chlorinated paraffin wax.

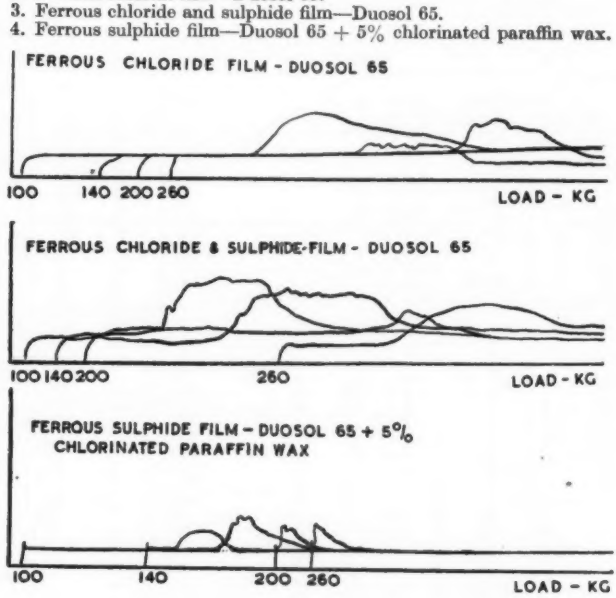


FIG. 4.

FRICTION-TIME CURVES.

other balls by treatment with ammonium sulphide after a preliminary acid wash (this treatment giving a thin but regular film.[2]) A ferrous chloride film was also prepared on top of a sulphide film. The film thickness could not be accurately controlled, but only those balls which were coated with a uniform film were used in the tests. The films used were of much greater thickness than those produced by the action of E.P. additives, and therefore the results are valid only for qualitative comparison. The results are shown in Figs. 3 and 4.

Note.—In the case of ferrous chloride films the wear spots on the test balls were oval in shape, not circular, as in the case of untreated balls, and this effect was particularly noticeable in the case of balls coated with a double film of chloride and sulphide. This elongation of the wear spots suggests the smooth and even wearing of the film, and this is confirmed by the period of delay before seizure occurs. The sulphide film gives smooth wear under all loads and decreases the amount of wear at high loads in comparison with an untreated surface.

Section 3. *The Effect of Hydrogen Chloride.*

Since hydrogen chloride is liberated during the reactions which form the surface film of ferrous chloride, a study of the effects due to its presence was deemed to be necessary. For this purpose a saturated solution of dry hydrogen chloride in Duosol 65 oil was prepared and tested using untreated balls and sulphide coated balls. The results are shown in Figs. 5 and 6.

Prutton, Turnbull, and Dlouhy (*loc. cit.*) have observed the liberation of hydrogen chloride on heating iron powder with chlorine additives alone and in presence of sulphur additives, but suggest that it is an unlikely reaction intermediate. The above results indicate that whilst dry hydrogen chloride forms a ferrous chloride film and shows E.P. properties at low loads, the film formed is not sufficient to carry the high loads borne by an oil containing a lower proportion of chlorine in the form of a standard E.P. additive. Attempts to measure the hydrogen chloride formed during tests on the Four-Ball Machine, by titration of the used oil, showed no measurable increase in acidity in the case of blends of chlorine additives in oil, but in the case of neat chlorinated paraffin wax an appreciable formation of hydrogen chloride occurred, and the results obtained confirm the findings of the above authors, obtained by heating of iron powder with the additive, and justify

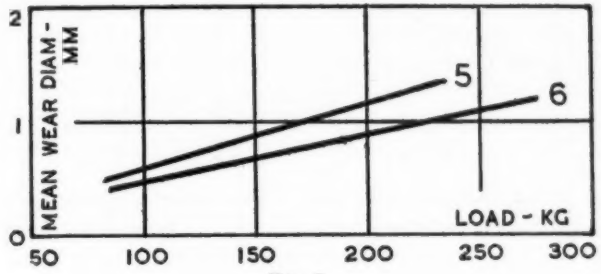
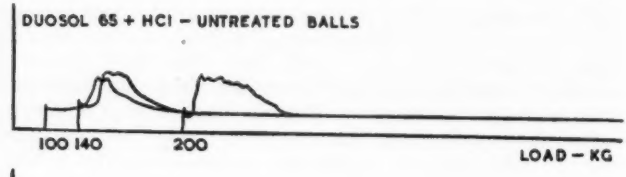


FIG. 5.

WEAR-LOAD DIAGRAM.

5. Duosol 65 + HCl, untreated balls.
6. Duosol 65 + HCl, sulphide film on balls.



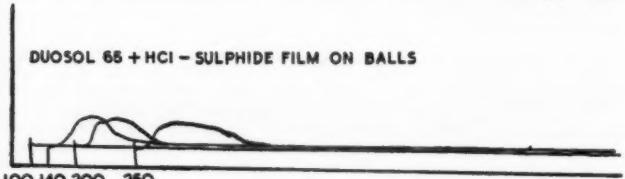


FIG. 6.

FRICTION-TIME CURVES.

their assumptions that high temperatures play an important part in the development of E.P. properties, and that the mechanism of additive decomposition by the action of heating or E.P. conditions are analogous.

The neutralisation-load curve for neat chlorinated paraffin wax is shown in Fig. 7.

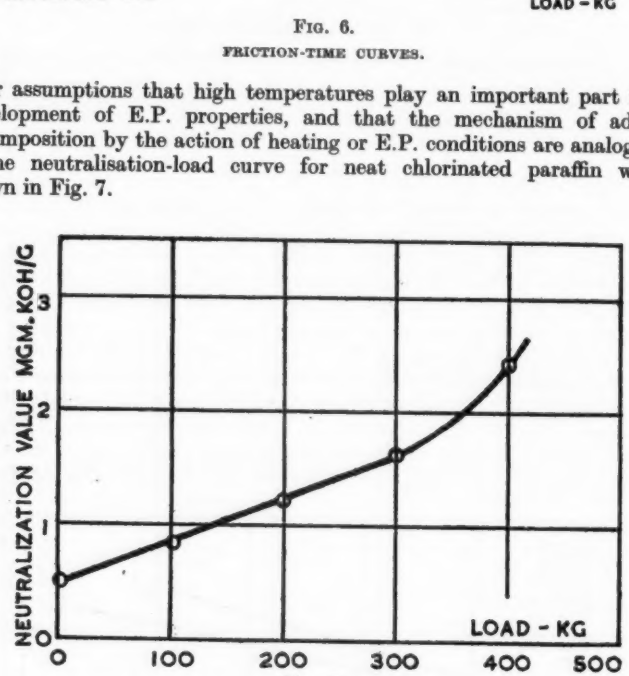


FIG. 7.

NEUTRALISATION-LOAD CURVE FOR NEAT CHLORINATED PARAFFIN WAX.

DISCUSSION OF RESULTS.

The results obtained in Section (1) give valuable confirmation of the value of the practice of using chlorine and sulphur additives together for E.P. lubricating conditions. The addition of sulphur has a most marked effect

on the blend of 5 per cent chlorinated paraffin wax—appreciably reducing the wear and lowering the frictional forces, particularly at high loads. The high peaks of the friction/time curves of 5 per cent chlorinated paraffin wax at loads of 260 and 300 kg are smoothed out by the addition of free sulphur. The effects produced by the addition of sulphur to benzotrichloride in oil are less marked than with chlorinated paraffin wax, but are quite clearly defined. Benzyl disulphide has a less pronounced effect than free sulphur, but this would appear due to its slower reaction with the iron surfaces to give a sulphide film.

The work of Section (2) on the effects shown by chloride and sulphide films shows clearly the part played by these films in the development of E.P. properties, and indicates that the ferrous chloride film (or that portion of a mixed film) is chiefly responsible for the E.P. effects, sulphur or a sulphide film assisting in the smooth wear of the chloride film and in the formation of this film from a chlorine additive and the iron surface.

The effects shown by hydrogen chloride in oil are of some interest, and indicate that it may react in two ways—when dry it can form a ferrous chloride film and show some E.P. effects, or when moist it can increase the wear by corrosion and lower the E.P. rating of a chlorine additive. The failure of hydrogen chloride in oil to carry a high load suggests that the chloride film is produced by the following stages, and not by the prior formation of hydrogen chloride :—

(*a*) formation of an addition complex by the chlorine additive and the iron surface,
(*b*) breakdown of this complex to form a ferrous chloride film,
(*c*) the formation of hydrogen chloride,

each of these stages being facilitated by sulphur or a sulphide film, indicating a free radicle or chain mechanism, which would be probable under the high temperature conditions operating.

In conclusion, this work gives confirmation of the results of Prutton, Turnbull, and Dlouhy using a different test apparatus, and indicates that the reaction mechanism proposed by them is the correct one.

ACKNOWLEDGMENT.

The author wishes to express his thanks to the " Shell " Refining and Marketing Co., Ltd., for the use of facilities to carry out the tests on the Four Ball Machine.

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[1] *J. Inst. Petrol.*, 1945, **31**, 73.
[2] *Ibid.*, 1945, **31**, 154.
[3] *Ibid.*, 1946, **32**, 90.

Acton Technical College,
High Street, Acton, W. 3.

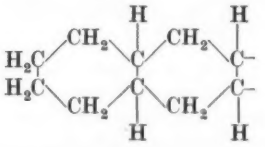
RESEARCHES ON ASPHALTENES. PART II. RADICAL REACTIONS.*

F. J. Nellensteyn, Ph.D., and J. Dorleyn.

In the colloid carbon theory of asphaltic bitumen published by the senior author, 1923,[1] dissociation products of the hydrocarbons (radicals) play a great part.

In this theory asphaltic bitumen is considered as a highly protected oleosole of carbon. The carbon kernels with the protective bodies form the micels, the oily constituents, the medium of these colloidal systems.

The colloidal structure of asphaltic bitumen, the micel-medium structure, is generally accepted, but views still widely differ as regards the inner structure of the micel. Mack[2] and others defend the theory that this asphaltic bitumen mical consists of highly polymerized hydrocarbons, probably compounds of the following constitution; combined by S and O bridges.



This constitution, which is improbable on account of the fact that a polymer character of asphaltic bitumen has never been proved, must be rejected in connection with the oxidation of the asphaltic bitumen micel by $KMnO_4$ to mellitic acid.

Pfeiffer and Saal[3] are in closer agreement with the authors in their view on the asphaltic bitumen problem. They accept, at least as probable, that the inner kernel of the asphaltic bitumen micel must consist of pure carbon, and that the H content of the micel, generally called asphaltenes, must be due to peripheric situated *chemically bound* hydrocarbon groups. According to the authors, this H content is originated from dissociation products of hydrocarbons, radicals, principally $:CH_2$ and $:CH$ groups and combinations of both. The chlorination of asphaltenes, carried out by Dorleyn in this laboratory should decide this.

Experimental.

The CS_2 soluble, ether insoluble compounds, the ether asphaltenes from Boeton asphalt, a natural asphalt from the Isle of Boeton in the Dutch East Indies, are extracted for 40 hours with ether, the bulk of the ether eliminated by evaporation in a steam bath, and the last traces of ether and water by leading a stream of dry pure nitrogen over the asphaltenes which

* Part I was published in *J. Inst. Petrol.*, 1940, **26**, 401–406.

are heated at 80° C to constant weight. The product shows the following characteristics :

Ultimate analysis :[4]

	Per cent.
C	77·6
H	8·1
S	9·6
N	0·7
Ash	1·3
O (by difference)	2·7
Carbon residue in a stream of hydrogen	22·0
H–C ratio of the protective bodies	1·7

These asphaltenes show a low H–C ratio; this means a rather high percentage of ⋮CH groups compared with other asphaltenes. The low percentage of the carbonization residue is characteristic for natural asphalts.

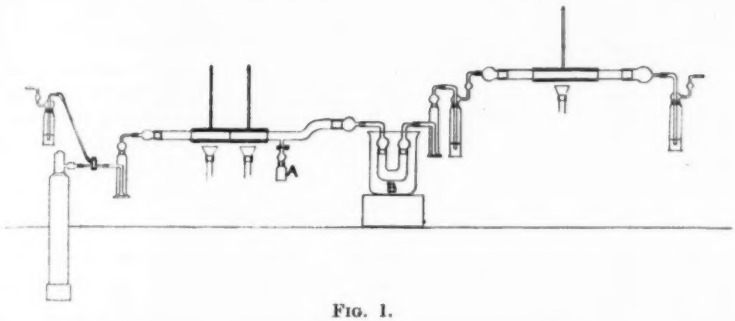


Fig. 1.

20-g asphaltenes are chlorinated in a hard glass tube (Fig. 1). The heavy fractions are collected in the small vessel, A, the light products pass a condenser B cooled by ice and salt. The non-condensed gases are led through water with H_2O_2. The chlorination is done in three stages :

At first chlorine is passed over the asphaltenes for 3 hours at a temperature from 200° to 400° C. Then the more or less carbonized asphaltenes are eliminated from the tube, powdered, and chlorinated again at 400° C for 3 hours. A third chlorination takes place at a temperature of 550° C.

The first chlorination is characterized by a violent reaction, which begins at 200° C, and the asphaltenes catch light; liquid and crystalline reaction-products are formed. The non-condensed gases react with water (H_2O_2 is not directly necessary for this reaction, but is added to secure a complete oxidation). The water becomes very hot; H_2SO_4 is formed in abundant quantities, and sometimes also sulphur.

At the second chlorination the formation of crystals preponderates; at the third the whole back side of the tube is filled with crystals. The reaction is not nearly so violent as the first chlorination.

The crystalline reaction products (Fig. 2) are purified by repeated sublimation; they contain a small percentage of oily products which are eliminated completely by heating at 110° C (Fig. 2). The purified crystals show a melting point of 227° C. The elementary analysis (24·6 per cent C;

74·7 per cent Cl and no H) and this melting point prove that the crystals are C_6Cl_6 (m. p., 227° C; C, 25·3 per cent, H, 0·0 per cent, Cl, 74·7 per cent).

From the oily reaction products individual chemical compounds could not be isolated. The products form a mixture of the following average composition:

	Per cent.
C	46·0
H	4·6
Cl	43·1
S	3·4
Ash	0·3
Molecular weight	474 [3]

The gaseous products are not completely converted into H_2SO_4 and other compounds by the H_2O_2 solution.

When drawing up the S balance-sheet it appeared that 49 per cent of the sulphur which reacted with chlorine was found in the oily products and 27 per cent as H_2SO_4 and S in the H_2O_2 solution. The rest could be converted into $MnSO_4$ by passing these products over MnO_2 at 400° C.

Taking carbon dioxide snow with ethanol as cooling agent instead of ice and salt, the results did not change. When cooling with liquid air, after cooling with carbon dioxide snow and ethanol, the reaction which led to the formation of H_2SO_4 in the H_2O_2 solution ceased, but the forming of $MnSO_4$ still took place.

Discussion of the Results.

The formation of C_6Cl_6 is a definite proof of the presence of mono-C atomic radicals in asphaltic bitumen. It is obvious that the following reactions take place:

$$:CH + Cl_2 \longrightarrow :CCl + HCl$$

$$6:CCl \longrightarrow C_6Cl_6$$

In the authors' original conception of the colloid carbon theory of asphaltic bitumen the following radicals (dissociation-products) may be expected:

$$:CH,\ :CH_2,\ \cdot CH_3 \text{ and higher radicals.}$$

Chlorination may lead to the formation of completely chlorinated radicals $:CCl$, $:CCl_2$ and $\cdot CCl_3$, and in the case of $:CH_2$, $\cdot CH_3$ and the higher radicals of incompletely chlorinated radicals—*e.g.*, $:CHCl$ and $\cdot CH_2Cl$.

Further formation of carbon may take place, recording to the reactions:

$$2:CH + Cl_2 \longrightarrow 2C + 2HCl \text{ or}$$

$$:CH_2 + Cl_2 \longrightarrow C + 2HCl$$

It is very probable that all these reactions take place, but the reactions with $:CH_2$, $\cdot CH_3$ and higher radicals are principally in the first stage of the chlorination, and the reaction $:CH + Cl_2 \longrightarrow :CCl + HCl$ especially during the second and third chlorination.

Owing to these circumstances the characteristic compound for the chlorination of $:CH$ radicals, hexachlorobenzene, may be rather easily isolated.

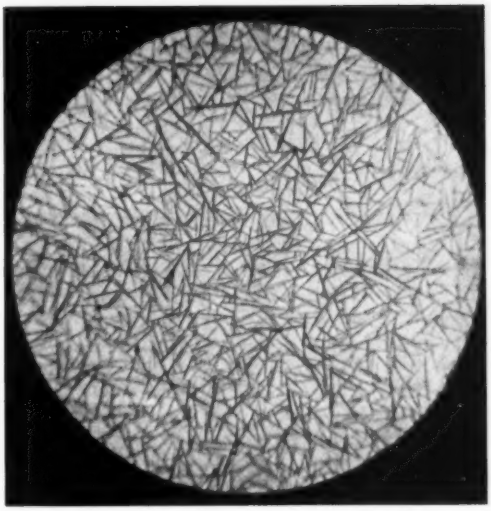


FIG. 2.

PURIFIED CRYSTALS, SUBLIMATED AT 110° C.

[*To face p.* 584.

The other chlorination products of the hydrocarbon radicals are found in the oily distillate, evidently a mixture of many compounds; this mixture also contains C_6Cl_6; there are indications of the presence of C_2Cl_4, the dimer of $:CCl_2$; lower-boiling products are also present.

It seems rather astonishing that the radicals with their unsaturated character show a preference for substitution in state of addition. The H-atoms, especially in the :CH, but also in the other radicals, are certainly very unstable; there is a tendency to form C and H; when liberated, they have a short life. If no substituting agents are present association of the radicals to various compounds takes place—*e.g.*, in the ordinary distillation.

Chlorine, however, easily substitutes the H-atoms in the decomposing radicals. The radicals :CH, $:CH_2$ and $\cdot CH_3$ must be considered as gaseous dissociation products, dissolved in the undissociating compounds; there is a certain similarity with the ion condition. It is possible that $:CH_2$ and $\cdot CH_3$ radicals are more volatile than the :CH radicals; the decreasing H–C ratio during the distillation of the higher bituminous substances is an indication in this sense. The formation of carbon, mentioned above, caused by the reactions:

$$2{:}CH + Cl_2 \longrightarrow 2C + 2HCl$$
$$:CH_2 + Cl_2 \longrightarrow C + 2HCl$$

occurs especially during the first stage of the chlorination; clouds of carbon are then formed.

These chlorination reactions show a marked resemblance with the formerly investigated reactions with oxygen and iodine.[6]

Very interesting are the mysterious reactions of chlorine with the sulphur compounds; although the nature of the reacting compounds and of the reaction products could not be identified as in the case of the reaction: $:CH \longrightarrow :CCl \longrightarrow C_6Cl_6$, the radical character of the S-reactions could be set beyond all doubt. The fact that most of these compounds pass carbon dioxide-ethanol (−78° C), and some of them even liquid air (−180° C) without being condensed, excludes the possibility that ordinary sulphur compounds play a part in these reactions, the more so as the absence of H_2S, the most volatile S-compound, could be proved by passing the gaseous products over lead acetate. The question is now which are the original S-radicals in the asphaltenes and into which products are they converted. In the vessels with dilute H_2O_2, S is formed principally as H_2SO_4, and a small part as elementary S. The reaction resembles in many respects the conversion of S_2Cl_2 into H_2SO_4 according to the scheme:

$$S_2Cl_2 + 8H_2O + 5Cl_2 \longrightarrow 2H_2SO_4 + 12HCl$$

combined with the reaction:

$$2S_2Cl_2 + 3H_2O \longrightarrow H_2SO_3 + 3S + 4HCl$$

H_2SO_3 being converted by H_2O_2 into H_2SO_4.

S_2Cl_2 itself cannot react here; it must be totally condensed by ice and salt, and certainly by carbon dioxide snow and ethanol. It is more probable that some S Cl radical—*e.g.*, S–Cl is the reacting compound. It must be noted that C-containing radicals are also present in the gaseous products. The nature of the S radicals in asphaltic bitumen, which are converted by

chlorine and the H_2O_2 solution into H_2SO_4 is still unknown. There are some indications that :CS radicals play a part which may be expected to be more or less stable, as is the case with the allied oxygen compound CO.

Finally, it may be mentioned that these reactions are not restricted to Beoton asphalt; a Mexican distillation residue gave similar results.

We wish to express our special thanks to Miss G. M. A. Steffelaar, Prof. Dr. Ir. H. I. Waterman and Ir. H. Gravestein for their valuable support.

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[2] C. Mack. *J. Physic. Chem.*, 1932, **36**, 2901; H. Walther. *Kolloid Z.*, 1942, **99**, 99.
[3] *J. Physic. Chem.*, 1940, **44**, 139.
[4] Nellensteyn en Steffelaar. *Chemisch Weekblad*, 1945, **41**, 5.
[5] W. Prahl. *Z. Angew. Chemie*, 1939, **52**, 431.
[6] J. Alexander. "Colloid Chemistry," 1931, vol. III, p. 535.

The Hague, Holland, June 1946.
State Road Laboratory.

ERRATA.

General Discussion on Transformer Oils, page 355. In the penultimate line of paragraph 4 the names "Dr. Wien" should read "Professor Weiss" and "M. Rogieres" should read "M. Roegiers."